THE MARANGONI EFFECT IN GAS ABSORPTION

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PREFACE

The work described in this dissertation was carried out in the Department of Chemical Engineering, University of Cambridge, from October 1974 to June 1977. It is the original work of the author, except where specifically stated in the text, and has not been carried out in collaboration with anyone else. Neither the present dissertation, nor any part thereof, has been previously submitted to any other university.

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SUMMARY

There exists plentiful evidence that in some gas-liquid systems interphase mass transfer, possibly accompanied by reaction, results in the occurrence of convective currents in the vicinity of the interface driven by gradients of surface tension - the Marangoni effect. This is a matter of some practical importance as it may give rise to mass transfer rates much higher than those predicted in ignorance of the Marangoni phenomenon. The occurrence of such convective currents in initially quiescent, or quasi-quiescent, systems is referred to as Marangoni instability.

The effect of Marangoni convection, induced by the desorption of acetone from dilute aqueous solutions into air, on the mass-transfer coefficients was investigated in a laboratory packed column and a novel stirred cell apparatus. It was observed that, in the range investigated, the liquid-phase mass-transfer coefficient was significantly enhanced, by as much as more than a factor of four in the case of the stirred cell, because of the Marangoni convection. By contrast, the experiments indicated that, in the range investigated, the Marangoni convection had virtually no effect on the gas-phase mass-transfer coefficient. In addition, an attempt has been made to elucidate the effect of the ratio of the mass transfer resistance in the liquid phase to that in the gas phase on the liquid-phase enhancement factor in the case of Marangoni convection induced by the desorption of solutes which depress the surface tension.

The rate of growth of Marangoni instability, induced by the desorption of acetone, was studied in a wetted-wall column. The experimental results appear to indicate that the growth of the instability to the fully-developed state occurred in a time very much smaller than the

exposure-time in the range studied.

An attempt has been made to rationalize the occurrence of Marangoni instability during the absorption of CO_2 into aqueous amine solutions. The rate of growth of the instability in this case was studied in a laminar jet apparatus. It was shown that, in the range studied, the effect of the ensuing Marangoni convection on the rate of absorption was significant even for exposure-times of the order of a few milliseconds. Experiments on the absorption of CO_2 into aqueous monoethanolamine solutions in the packed column, however, showed no evidence of the occurrence of any Marangoni convection. Some reasons which may account for this anomalous result have been discussed.

Finally, the possibility of the a priori prediction of the intensity and scale of the Marangoni convection in the cellular convection regime was investigated.

CHAPTER ONE

INTRODUCTION

1.1 General Considerations

A knowledge of the mechanism of mass transfer across fluid-fluid interfaces is of fundamental importance in the design of industrial separation processes such as absorption, extraction, and distillation. Because of its relative importance, interfacial mass transfer has been extensively studied, and several theories have been proposed to model the phenomenon of interfacial mass transfer. Most of the theories assume that in the close vicinity of the interface, mass transfer occurs as a result of molecular diffusion, and that at the interface the two phases are, at all times, in thermodynamic equilibrium. The first assumption has been verified experimentally, even in systems exhibiting a high degree of turbulence in the bulk of the fluid phases. The assumption of thermodynamic equilibrium has also been verified for gas-liquid systems in the absence of a film of contaminant molecules at the interface and under conditions usually encountered in practice. It is in general also valid for liquid-liquid systems, although some liquid-liquid systems appear to exhibit a surface resistance to transfer even in the absence of a contaminant surface film.

In most cases of interfacial mass transfer, the transport processes occurring at the interface have relatively little influence, if any, on the hydrodynamics of the adjacent fluid phases. In other words, the fluid-mechanical description of the system under investigation is essentially unchanged by the transport of matter across the interface. Under some circumstances, however, the fluid mechanics of the system

can be radically altered by the transfer process occurring at the interface. As a result of interfacial mass transfer, secondary convection currents may arise in the vicinity of the interface. Such convection currents, in general, have a profound effect on the rate of mass transfer.

Convection currents at the interface may be due to the formation of an unstable density gradient arising as a result of the transfer process, with heavier fluid residing on the top of less dense fluid within the same phase. This type of instability is commonly referred to as Rayleigh instability [B4]. In addition, fluid motion at the interface can occur as a result of the presence of a gradient of interfacial tension in the plane of the interface. The occurrence of a gradient of interfacial tension along the interface is in general the manifestation of a gradient of solute concentration or temperature normal to the interface, i.e. a gradient of "inherent" interfacial tension normal to the interface. An interfacial-tension gradient is manifested as a shear stress acting in the plane of the interface [S9]. The various influences of such a gradient of interfacial tension on the hydrodynamics of the adjacent fluid phases are collectively termed the "Marangoni effect". In this dissertation, we shall be concerned solely with the influence of the Marangoni effect on mass transfer across gas-liquid interfaces. Furthermore, the analysis will be restricted to Newtonian liquids.

The shear stress resulting from a gradient in surface tension can act as a prime-mover and initiate motion in quiescent or quasi-quiescent systems, or it can interact with already existing motion at the interface. In the case of gas-liquid systems commonly encountered in practice, the equilibrium surface tension is a function of solute composition, solute concentration, and temperature. For the sake of

clarity, the following discussion will be restricted to a system consisting of two immiscible gas and liquid phases, and a solute which is transferred between them across a common interface. Density effects are assumed to be negligible. Hence, within this framework, a gradient of surface tension implies a variation from point-to-point of concentration or temperature at the interface.

A variation of solute concentration or temperature at the surface during interphase mass or heat transfer can, in general, arise in one of the following ways.

1. As a result of fluid eddies having a different solute concentration or temperature from that existing at the surface, reaching or approaching the surface from the bulk of the fluid phase.

2. As a consequence of the flow of the two phases relative to each other, or due to geometrical non-uniformity of the two phases about the interface, e.g. the case of a curved meniscus or a liquid film which is locally thin or thick, or through the presence of point sources of solute or heat in the surface.

3. Due to the spontaneous growth of ever-present random infinitesimal local fluctuations in surface tension (due to fluctuations in solute concentration or temperature) at the interface. In this case, the resultant convective motion is referred to as "Marangoni instability".

In the last case, the resulting convective motion is also commonly referred to as "interfacial turbulence". This usage is misleading since the convective motion is not necessarily turbulent, and hence the use of the term interfacial turbulence will be avoided in this dissertation.

The convective motion due to the Marangoni effect will in general result in an increase in the rate of transport of the solute between the two phases. In some cases, the Marangoni convection can profoundly

affect the interfacial area of contact between the two phases. In gas-liquid systems, the surface tension is in general much more sensitive to changes in the concentration level of the solute than temperature changes. Hence in non-isothermal systems, the surface stresses generated by variations in the concentration of the solute at the surface are in general much greater than the stresses generated by the simultaneous temperature variations.

1.2 Origin of Marangoni Instability

Consider the gas-liquid system shown in Figure 1-1. For simplicity, temperature and density effects are assumed to be negligible and, moreover, the discussion will be limited to a two-dimensional system. The gas phase (phase A) is assumed to be immiscible with the liquid phase (phase B). Initially, the liquid contains a dissolved solute S, the concentration of which is uniform throughout the liquid phase. The gas phase is assumed to be initially solute-free. On contacting the two phases, the solute S is transferred from the liquid phase into the gas phase. Figure 1-1a shows the system at an instant in time subsequent to the contacting of the two phases. Because of the presence of random infinitesimal fluctuations in concentration, always present in real systems, the concentration of the solute will not be uniform everywhere at the interface and a point-to-point variation will exist. As a consequence, areas of infinitesimally high and low surface tension will occur. These areas of low and high surface tension are represented in an idealised form by the points a and b, respectively, in the figure. The resulting infinitesimal shear stresses will give rise to minute flows as indicated in Figure 1-1b. Areas of low surface tension will expand and those of high surface tension contract.

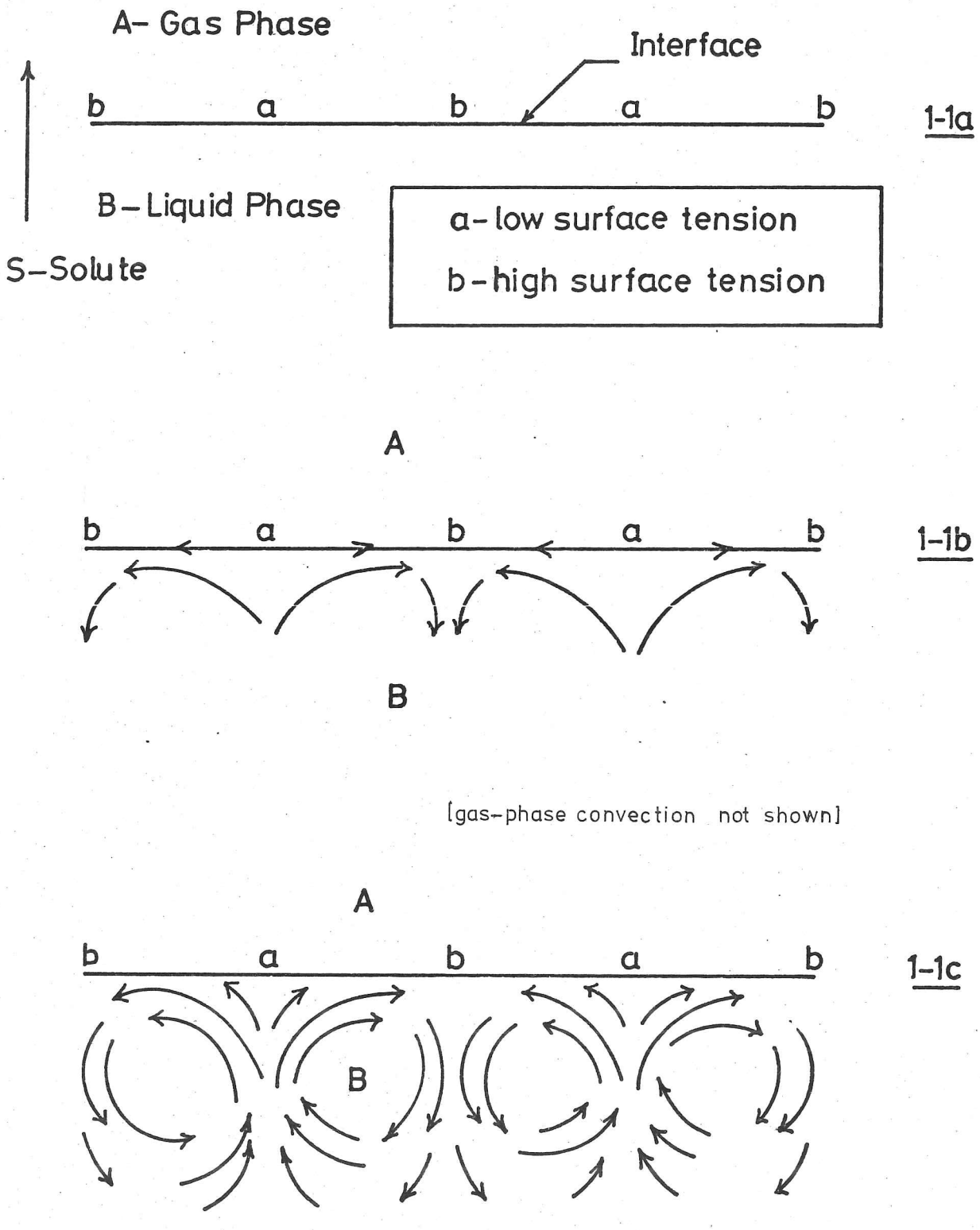

FIG. 1-1 Schematic Representation of the Development of Marangoni Instability

The reaction of the system to these minute flows determines, in effect, the stability of the system. If the ensuing flow results in a concentration gradient along the interface which reinforces the original gradient responsible for the flow, the original disturbance will be progressively amplified and give rise to macroscopic convective motion. This type of instability is called "stationary" instability. If, however, the ensuing flow does not reinforce the original gradient, the motion will be damped owing to viscous forces and the system will be stable with respect to infinitesimal disturbances. This will also be the case in general when the ensuing motion results in surface stresses which oppose the original infinitesimal disturbance. If, however, the induced opposing gradient is large enough to result in a reversal of the original flow, the flow in the reverse direction being of greater intensity, a macroscopic to-and-fro motion at the interface will result. This type of instability is commonly referred to as "oscillatory" instability or overstability [S2,S9].

In initially quiescent systems, provided that the driving force for instability is not excessively large, stationary instability generally results in relatively ordered "cellular" convective flow, shown schematically in Figure 1-1c. The distinct individual patterns of flow shown in the figure are commonly referred to as "convection cells".

Considerations similar to those discussed above are also applicable to cases where the transfer of the solute is accompanied by a simultaneous chemical reaction in the liquid phase, e.g. the absorption of carbon dioxide into aqueous amine solutions (see Chapter Six).

The stability of a system with respect to infinitesimal disturbances can be investigated theoretically by using the technique of linear hydrodynamic stability analysis [L6]. This method is described briefly in the

following chapter of this dissertation. In the case of the air-water system, if a solute such as acetone which depresses the surface tension in solution is desorbed from water into air, the theory predicts that under certain conditions the system will exhibit stationary instability.

Care must be exercised in the analysis of systems which are susceptible to both Marangoni and Rayleigh instabilities. The Marangoni and Rayleigh instabilities are tightly coupled, and in such systems the density gradients may exert a strong influence on the form of the fully developed convection [B5,N2].

1.3 Aim of the Present Investigation

The ultimate goal of research into the Marangoni effect is the *a priori* prediction of the conditions under which Marangoni convection will occur for a given system, and the effect of the convective motion on the rate of mass and/or heat transfer across the interface. Quantitative prediction of the effect of Marangoni convection on the rate of mass transfer requires the ability to predict the morphology of the convective flow and its intensity, possibly as a function of time, from first principles.

It is hoped that the experiments presented in this thesis, together with the accompanying analyses and speculations, represent an appreciable contribution towards the realisation of the above stated goal.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Although the fact that gradients of surface tension can produce strong convective motion at the interface was established more than a century ago, e.g. the elucidation of the occurrence of "tears" of wine in a goblet containing wine [B4], a systematic study of the mechanism, occurrence, and effect on interfacial mass transfer of surface-tension driven flows was initiated only some twenty-five years ago. Most of the previous work deals with the effect of Marangoni convection in liquid-liquid systems, and is summarised in excellent reviews by Sawistowski [S1,S2,S3] and Berg [B5]. Quantitative investigation of the effect of Marangoni convection in gas-liquid systems has only just begun. The previous published work can be conveniently subdivided into two broad categories: 1) theoretical investigations; and 2) experimental studies. Previous experimental work on the effect of Marangoni convection in gas-liquid systems is reviewed below subsequent to a review of the relevant theoretical work.

2.2 Previous Theoretical Work

2.2.1 Linear Stability Analyses

Most of the theoretical analyses carried out have made use of the technique of linear hydrodynamic stability analysis with a view to determining the conditions under which the system investigated would exhibit Marangoni instability. Linear hydrodynamic stability analysis was used to examine the fate of infinitesimal disturbances once they

occurred in the steady or quasi-steady unperturbed initial state (random infinitesimal fluctuations of system variables always occur in real systems). The system was hydrodynamically stable if the infinitesimal perturbations were found to decay with time subsequent to initiation, and unstable if the perturbations were shown to grow with time.

The technique essentially examines the fate of the infinitesimal disturbances, as described by perturbations in all the system variables, by solving the appropriate equations of change subject to the relevant boundary conditions. Extreme care must be exercised in the choice of the boundary conditions if the practical utility of the analysis is not to be put seriously in doubt. What is actually determined in most cases is the state of the system, as described by the pertinent dimensionless groups, corresponding to "neutral stability" wherein the disturbances neither grow nor decay with time. The values of the dimensionless groups corresponding to a non-trivial solution for the state of neutral stability demarcate stable from unstable states of the system. The complete theory is discussed elsewhere in the literature [B4,L6].

The fact that Marangoni instability is a consequence of the hydrodynamic instability of the system to infinitesimal perturbations was first shown theoretically by Pearson [P1]. He used linear stability analysis to examine the stability of a thin quiescent layer of liquid, infinite in lateral extent and heated from below. The upper surface of the liquid was in contact with a quiescent gas phase. The unperturbed temperature profile was assumed to be linear, and the gas-liquid interface was assumed to be planar and inflexible. Surface viscosity and elasticity were assumed to be negligible. Pearson showed conclusively that for the above system the cellular convective motion observed, which had earlier been attributed to the action of buoyancy forces, could be

induced and driven by surface-tension forces arising due to temperature gradients in the case analysed (it should be pointed out, however, that Block [B7] by means of a few simple but elegant qualitative experiments had arrived at a similar conclusion a couple of years before Pearson published his work). Moreover, it was shown that surface-tension forces were the likely cause of convective motion observed in systems which were stable with regard to buoyancy forces. In the analysis, the gas-phase heat transfer was modelled by a constant heat-transfer coefficient, and oscillatory instabilities were assumed to be absent. The latter assumption was verified by Vidal and Acrivos [V1]. An important finding was that, for the model investigated, the temperature gradient in the unperturbed state must exceed a certain critical value, the magnitude of which depends on the properties of the liquid, the liquid depth, and the value of the heat-transfer coefficient at the gas-liquid interface, for instability to manifest itself, in agreement with the original experiments of Bénard [cited in B4].

In their independent, comprehensive, and pioneering study Sternling and Scriven [S9] examined the stability of a fluid-fluid system during the transfer of a solute across a common interface. The model studied consisted of two immiscible semi-infinite quiescent fluid phases in contact along a plane inflexible interface. The phases were assumed to be in thermal equilibrium. Interphase mass transfer of a single solute, in the absence of chemical reaction, was studied. The properties of the two fluids were assumed to be constant and independent of solute concentration. The equilibrium interfacial tension was assumed to vary linearly with concentration of the solute in the liquid. In the unperturbed state, the concentration gradients of the solute normal to the interface in the two phases were assumed to be linear and to extend

throughout each phase. Their analysis showed that some systems may be stable with solute transfer in one direction yet unstable with solute transfer in the reverse direction. It was concluded that for the commonly encountered case where an increase in solute concentration decreases the interfacial tension, Marangoni instability is favoured by:

1) solute transfer out of the phase of higher kinematic viscosity;

2) solute transfer out of the phase of lower diffusivity;

3) large differences in the kinematic viscosity and/or solute diffusivity between the two phases;

4) steep concentration gradients in the vicinity of the interface;

5) large absolute value of the rate of change of interfacial tension with respect to the bulk concentration of the solute;

6) low absolute values of viscosities and diffusivities in both the phases;

7) absence of extraneous surface-active agents.

These conclusions lead to the oft-quoted Sternling and Scriven criterion that, for the case where interfacial tension decreases with increasing solute concentration, instability is promoted by diffusion of the solute out of the phase of higher kinematic viscosity and/or lower solute diffusivity. Thus, if both the kinematic viscosity and solute diffusivity are lower in either one of the two phases, the system is unstable with transfer in either direction.

In the case of the air-water system, the solute diffusivity is much higher in the gas phase. In addition, the kinematic viscosity of

the gas phase is an order of magnitude greater than that of the liquid phase. If a solute such as acetone which depresses the surface tension is transferred between the phases, the above theory predicts that transfer from the liquid into the gas phase is susceptible to stationary instability, and that transfer in the reverse direction is susceptible to oscillatory instability.

Ruckenstein and Berbente [R3] extended the analysis of Sternling and Scriven for the case of mass transfer accompanied by a first-order chemical reaction. It was shown that even small values of the reaction rate-constant drastically altered the circumstances in which convective instability occurred. Gross and Hixson [G1] extended the Sternling and Scriven analysis to include unsteady-state diffusion and interfacial resistance. They showed that in the presence of interfacial resistance the system is unstable to transfer in either direction. Various other extensions of the Sternling and Scriven theory are discussed elsewhere in the literature [I1,S1].

Scriven and Sternling [S4] extended the work of Pearson to include a flexible interface. It was concluded that a deformable surface is susceptible to Marangoni instability over a much wider range of parameters relative to an inflexible interface. They further showed that the morphology of the convective motion could be used to distinguish between buoyancy driven and surface-tension driven flows. It was shown that in the case of surface-tension driven flows, the points at which the liquid from the interior reaches the surface are depressed relative to the points at which the liquid re-enters the bulk. In the case of buoyancy-driven flows, the reverse has been found to be true. The conclusion with respect to surface-tension driven flows had been arrived at earlier by Hershey [H1], using less rigorous arguments. In a complementary paper,

Smith [S8] showed that by taking account of gravity waves in the analysis (especially important at small wave-numbers), several ambiguities in the previous paper could be resolved.

Nield [N2] examined the stability of the Pearson model when subject to destabilising buoyancy and surface-tension gradients. It was shown that the two mechanisms are tightly coupled and reinforce each other.

Berg and Acrivos [B3] studied the effect of extraneous surface-active agents on Marangoni instability. Using the model of Pearson, they showed that even minute traces of surface-active agents exert a profound stabilising effect on convection driven by gradients of surface tension. This result is of significance for air-water systems which are particularly prone to contamination by extraneous surface-active agents. The presence of contaminants was shown to give rise to an apparent surface elasticity with consequent stabilisation.

An interesting example of the inhibition of surface motion by the presence of surface-active agents is the reduction in the rate of oxygen uptake in rivers, due to a decrease in the rate of surface renewal by turbulent eddies, as a consequence of contamination by non-degradable household detergents.

It had been originally suggested by Pearson that his theory could be applied without significant change to the analogous mass transfer problem. The only modification required would be the substitution of the dependence of surface tension on temperature by its dependence on concentration. However, the modified theory agreed poorly with the experimental results as far as the onset of convective instability was concerned. Brian [B12] proposed that this discrepancy could be due to the effect of the "Gibbs adsorption layer", formed by the adsorption at the gas-liquid interface of solute molecules which depress the

surface tension in accordance with the theory of Gibbs. In the case of solutes which depress the surface tension, there occurs a relative increase in the concentration of the solute in the immediate neighbourhood of the surface, and this much enhances the reduction of surface tension compared to that which might be expected from the concentration of the solute in the bulk of the liquid.

Brian investigated the mass transfer analogue of the problem studied by Pearson, i.e. the desorption from the liquid phase into the gas of a solute which lowered the surface tension, taking into account the adsorption of the solute at the surface. The mass transfer in the gas phase was represented by a constant gas-phase mass-transfer coefficient.

An important dimensionless parameter which is encountered in theoretical analyses of Marangoni instability in gas-liquid systems is the Marangoni number (N_{Ma}). The Marangoni number is a dimensionless group which can be interpreted as being proportional to the ratio of the destabilising surface-tension forces to the stabilising viscous forces. A given system, for a given set of conditions, will be unstable with respect to infinitesimal perturbations provided that the value of the Marangoni number exceeds a minimum value called the "critical" Marangoni number.

In the case analysed by Brian, it was shown the value of the critical Marangoni number was strongly dependent on the surface concentration of the solute in the Gibbs adsorption layer, the surface concentration being represented in the analysis in a dimensionless form called the Adsorption number (N_{Ad}). The Adsorption number was defined as the ratio of the surface concentration of the solute in the Gibbs adsorption layer to the product of the depth of the liquid layer and the

concentration difference of the solute across the liquid layer. It was shown that the presence of the Gibbs adsorption layer resulted in a large increase in the value of the critical Marangoni number. The analysis assumed that oscillatory instability could be neglected in determining the state of neutral stability. This was subsequently verified by Brian and Smith [B13].

Brian and Ross [B14] extended the above analysis, and used a "broken-line" profile for the unperturbed concentration profile, i.e. the concentration was assumed to vary linearly with depth upto a finite "penetration" depth and was assumed to be constant thereafter. This type of profile had been used earlier for the analogous temperature-driven case by Vidal and Acrivos [V2]. The model was claimed to be more realistic than those previously investigated, and could be applied to mass-transfer induced instability in laboratory apparatus such as laminar-jet absorbers and wetted-wall columns. Results were obtained for various ratios of liquid layer thickness to mass-transfer penetration depth. For deep pools, it was shown that complete stabilisation occurred for Adsorption numbers in excess of 0.5, irrespective of the shape of the unperturbed concentration profile in the liquid or the liquid-to-gas phase resistance ratio. The definition of the Adsorption number used in this work was a slightly modified version of the definition in Brian's previous paper; in the modified version, the depth of the liquid layer was substituted by the mass-transfer penetration depth. They showed further that in general the critical Marangoni number increased with an increase in the liquid-to-gas phase resistance ratio, and also with an increase in the Adsorption number. The analysis reduced the discrepancy between the values predicted theoretically and determined experimentally for the critical Marangoni number in the case of desorption of triethyl-amine from aqueous solutions by a factor of approximately 1000.

Shah and Szeri [S5] studied the stability of gas-liquid systems for absorption accompanied by chemical reaction and large heat effects. They postulated that such systems were potentially unstable if, as a result of interfacial heat transfer, the temperature at the interface is lower than that in the sub-interfacial layers. The results were used to qualitatively explain the instability observed during the absorption of chlorine into toluene. However, in the absence of solvent evaporation, it is likely that heat transfer to the gaseous environment would have to be unrealistically high to result in a destabilising temperature gradient at the gas-liquid interface.

Wang, Ludviksson, and Lightfoot [W1] investigated the stability of vertical laminar falling films subjected to interphase mass transfer and an overall surface-tension gradient in the direction of flow. The results were found to confirm qualitatively the findings of several previous investigators [B5,B8,N3] in connection with the break-up of thin films into rivulets in the presence of interfacial mass transfer.

2.2.2 Miscellaneous Theoretical Work

Linear stability analysis has been employed to study the stability of a system to random infinitesimal perturbations. However, a gradient of interfacial tension along the surface can also arise in several other ways, the hydrodynamic consequence of which is not to be classed as Marangoni instability [see Chapter 1]. Several investigators have studied the effect of an overall gradient of surface tension on the convective-diffusion process. For example, Ruckenstein [R4] analysed the effect of an overall surface-tension gradient on the intensity of circulation currents inside moving drops and bubbles. Similar analyses have been carried out for laminar liquid films subject to overall surface-tension gradients in the direction of flow [L2,M2].

Some attempts have also been made to formulate a model for mass transfer in the presence of stationary Marangoni instability [B1,L4,R5, R6]. The fluid motion arising from the Marangoni instability has been idealized, in all the above analyses, as two-dimensional convection cells similar to those shown in Figure 1-1c. Though unrealistic from a physical standpoint, this idealisation of the motion by two-dimensional convection cells represents a convenient starting point for initial analyses, and is of help in laying the groundwork for further more complex analyses.

2.3 Previous Experimental Work

Previous experimental work can be broadly classified into two categories: 1) qualitative studies; and 2) quantitative work. Qualitative investigations have dealt with the qualitative confirmation of the predictions of linear stability analyses, and the use of optical techniques to investigate the morphology of the convection patterns established. Quantitative work has dealt, in the main, with the effect of Marangoni instability on the rates of mass transfer, mostly in simple laboratory contactors where the fluid-phase hydrodynamics is simple and well-defined in the unperturbed state.

2.3.1 Previous Qualitative Work

Two methods have been principally employed for the purposes of flow visualisation: 1) use of suspended particulate matter; and 2) optical techniques. For optical studies the interferometric, schlieren, and the shadowgraph systems have been commonly employed. These methods are based on the variation of the refractive index of the liquid with solute concentration or temperature, and have been adequately described in the literature [B4]. Most of the work has dealt with quiescent liquid-liquid

systems, and is covered in several reviews [B5,S1]. The morphology of the fully-developed convective motion due to Marangoni instability, provided that the destabilising gradients are not unusually large, is generally cellular in nature. The convection cells, viewed in a direction normal to the plane of the interface, are usually polygonal, with the fluid flowing within each cell from the centre outwards towards the periphery. In the presence of oscillatory instability, the cells may undergo periodic contraction and dilation. In general, there exists a distribution of cell sizes. The mean cell size has been found to be a function of solute concentration, although the precise dependence has not been unambiguously established. Furthermore, for thin liquid layers, it appears that the cell size increases with an increase in the depth of the liquid layer upto a critical value beyond which the liquid can be considered to be effectively infinite in depth [B4].

Linde et al. [cited in S1,L3] studied the occurrence of Marangoni instability in a wide variety of initially quiescent gas-liquid systems, both aqueous as well as non-aqueous. The results obtained were in satisfactory agreement with the predictions of linear stability analysis. During the desorption of ethanol into air from a 40 per cent aqueous solution in a simulated two-dimensional apparatus, clearly defined cellular convective motion was observed using suspended particles for flow visualisation. In the experimental apparatus used, a thin vertical layer of liquid was held between two vertical glass plates spaced only 0.25 mm apart.

Danckwerts and da Silva [D1] observed convection currents in a drop of 1 M monoethanolamine over which a gas stream of pure carbon dioxide was passed. Suspended particles were used for flow visualisation, and the convection currents observed directly using a microscope. It was

suggested that the instability resulted from the formation of ionic products at the interface due to the reaction between CO_2 and monoethanolamine, which gave rise to a substantially higher surface tension at the surface than that corresponding to the bulk liquid.

Thomas and Nicholl [T3] used a wave-front-shearing interferometer to investigate the occurrence of interfacial convection in the CO_2-monoethanolamine system in a stagnant pool of liquid. It is likely, for reasons stated subsequently, that the surface of the liquid in their experiments was contaminated, and that the observed convection was the result of an adverse density gradient. This may explain the relatively long exposure-times observed (4 - 20 seconds) for the manifestation of convective instability.

Thompson [T4] used the shadowgraph technique to observe the occurrence of convective instability in several initially quiescent gas-liquid systems. Convective instability was observed during the absorption of CO_2 into 2 M sodium hydroxide, SO_2 into water, and desorption of ethyl ether into air from a saturated aqueous solution. In some of the experiments, extremely fine-mesh screens, situated at the interface, were used to restrict the mobility of the gas-liquid interface. In other experiments a surface-film of contaminant was formed by deliberately adding a sufficient quantity of long-chain alcohols to the liquid pool. Rates of mass transfer were measured in the absence as well as in the presence of the screens and the surface-active agents. From the results it was concluded that instability during the desorption of ether was surface-tension driven, while in the other systems instability occurred due to buoyancy effects.

Berg et al. [B4] used the schlieren technique to observe convective flows during the evaporation of initially stagnant pools of pure volatile

liquids into a gaseous environment. In the case of non-contaminated thin liquid layers, the pattern observed was that of irregular polygons and, moreover, the size of the cells increased with an increase in the depth of the liquid layer. The patterns for deep pools were reported to be considerably more complex. It should be noted that the systems studied were unstable with respect to both density and surface-tension gradients. For very thin liquid layers density gradients are generally unimportant [P1]. However, the effect of buoyancy forces becomes more significant as the depth of the liquid layer increases. For liquid-liquid systems, it has been observed [B5] that the presence of a destabilising density gradient, during interfacial-tension driven convection, can alter the structure of the convective flow. The convective flow in such cases was observed to penetrate more deeply into the bulk of the fluid phases.

Published information on the morphology of Marangoni convection in flow systems is scanty. Gumerman and Hornsy [G2] studied the convective motion in a liquid-liquid system in a horizontal laminar-flow contactor. The interface was observed to be covered with "circular-shaped" convection cells, which were swept along in the direction of the bulk fluid motion. At low solute concentrations, the cells were observed to oscillate in size at a low frequency. The oscillation was found to be a flow-induced effect; when the flow through the contactor was stopped, the oscillation ceased. Mayr [M2] was able to observe the convective motion with the naked eye, under a narrow range of experimental conditions, during the desorption of triethylamine from water into a nitrogen gas stream in a short wetted-wall column. The entire surface was observed to be covered with polygonal cells which were observed to originate at the inlet distributor, and which were then swept along with the flow.

The analysis of Sternling and Scriven [S9] showed that, under certain

circumstances, the absorption of a solute such as acetone from air into water should result in oscillatory convective instability. This prediction appears to have been confirmed qualitatively by Linde et al. [L3]. Ellis and Biddulph [E1], and Ramshaw and Thornton [R1] have also reported the occurrence of convection currents during the absorption of solutes which depress the surface tension from air into water. Ripples of appreciable magnitude were observed at the gas-liquid interface during the absorption of acetone from air into water.

The results of investigations on the occurrence of Marangoni convection in stagnant gas-liquid systems should be analysed with due care. Liquid surfaces in such systems tend to become contaminated because of the accumulation of relatively insoluble surface-active agents at the interface, as a consequence of Gibbs' adsorption law, rendering the surface more-or-less rigid. This problem is particularly severe in aqueous systems because of the relatively high surface tension of water. The effect of contaminants is generally small when organic solvents of low surface tension are used.

2.3.2 Previous Quantitative Work

In their pioneering paper Brian, Vivian and Matiatos [B9] showed the occurrence of convective instability during the absorption of CO_2 into aqueous monoethanolamine solutions in a short wetted-wall column. Propylene, used as an inert tracer, was desorbed from the liquid during the simultaneous absorption of CO_2 to monitor the value of the liquid-side mass-transfer coefficient, k_L. The value of k_L was observed to be substantially increased, by as much as an order of magnitude, by the absorption-reaction process. It was proposed that Marangoni instability was the cause of the observed enhancement. For monoethanolamine concentrations greater than 0.5 M and with the gas phase composed of essentially

pure CO_2, the convection was observed to be so intense as to result in almost complete stripping of the propylene from the liquid phase in the short wetted-wall column.

Furmer et al. [F1] studied the effect of convective instability in a wetted-wall column in the ripple- and turbulent-flow regimes. The CO_2-MEA (monoethanolamine) system was investigated. Nitrous oxide was desorbed simultaneously during the absorption of carbon dioxide to measure the values of k_L. The enhancement of k_L was observed to be a monotonically increasing function of CO_2 concentration in the gas phase for a fixed MEA concentration in the liquid phase. The liquid phase Reynolds number was varied from approximately 340 to 2400. In the range of variables investigated, the maximum enhancement observed was approximately a factor of six.

Smigelschi, Suciu and Ruckenstein [S7] measured the rate of absorption of CO_2 into water under the influence of artificially generated macroscale convective motion at the interface. The gas-liquid interface was planar and horizontal, and radial movements were generated by continuously introducing at the centre of the liquid surface, via a capillary tube, miscible or partially miscible liquids which lowered the surface tension. A continuous flow of water was maintained through the contactor, and the surface was kept free of contaminants by using an ingenious weir device. A theoretical analysis, using experimentally determined velocity profiles, was shown to give predictions in good agreement with the experimentally observed enhancement of the rate of mass transfer.

Clark and King [C1] measured the rate of desorption of carbon disulphide, n-pentane, cyclopentane, and ethyl ether from n-tridecane into a flowing nitrogen gas stream in a laminar-flow horizontal contactor.

The rate of transfer of CS_2 was found to be in good agreement with predictions of the convective-diffusion theory for low CS_2 concentrations. However, for all the other solutes the rate of mass transfer was found to be much higher than that predicted theoretically, presumably as a result of convective instability. By computing the appropriate Rayleigh and Marangoni numbers, it was deduced that the enhancement observed in the rate of mass transfer was caused by Marangoni instability. Their calculations also appeared to indicate that the value of the gas-phase mass-transfer coefficient, k_G, was virtually unchanged by the occurrence of convective instability.

Brian, Vivian and Mayr [B11] studied the effect of Marangoni instability, caused by the desorption of solutes which lowered the surface tension, on the rate of mass transfer in a short wetted-wall column. Acetone, ether, triethylamine, and methyl chloride were desorbed from dilute aqueous solutions (less than 1 wt. %) into a countercurrent N_2 gas stream. The transfer process in each phase in the presence of convective instability was monitored by the simultaneous transfer of tracer solutes. Propylene (liquid-film controlled desorption) was desorbed to monitor the values of k_L, and the rate of transfer of water vapour was measured to monitor the values of k_G. It was observed that the value of k_L was enhanced by as much as 3.6-fold under the conditions investigated. However, as in the work of Clark and King, the values of k_G were found to be essentially unchanged by the occurrence of Marangoni instability. The experimentally determined values of the critical Marangoni number for each of the solutes studied were found to be much larger than those predicted theoretically using stability theory.

Clegg and Mann [C2] measured the rate of absorption of chlorine into a laminar liquid jet of carbon tetrachloride. A continuous stream

of chlorine was passed through the jet apparatus. The measured rate of absorption was found to be greater than that predicted by penetration theory. Moreover, the enhancement was found to be independent of the exposure-time of the liquid calculated on the basis of the jet length and the jet velocity. It seems likely that the convective instability was caused by the evaporation of the carbon tetrachloride into the chlorine gas stream.

Vivian and Brian [V4] reported some preliminary data on the effect of Marangoni instability on the rate of mass transfer on a sieve tray. Acetone was desorbed from dilute aqueous solutions into air to initiate Marangoni convection, and propylene was simultaneously desorbed to monitor the values of k_L. An increase in the concentration of acetone in the liquid from 0 to approximately 2 wt. % resulted in an increase in the point-efficiency for propylene desorption by about 50%. The point-efficiency for acetone desorption (gas-film controlled) was found to be virtually unchanged over the range of the variables investigated. The results reported are subject to some uncertainty, however, because the interfacial area of contact in sieve trays is known to be significantly altered by changes in the composition of the liquid on the tray as well as changes in the physical properties of the liquid on the tray.

Bond and Donald [B8], and Norman and Soloman [N3] studied the break-up of thin flowing liquid films during absorption of solutes which depress the surface tension, e.g. NH_3, ethanol, into water. It was found that the value of the minimum wetting rate, i.e. that value of the liquid flow rate required to form a continuous film over the entire supporting surface, increased as a consequence of the interfacial mass transfer. It was proposed that break-up of the liquid film was caused by surface-tension forces generated as a result of the relative accumulation of the solute at locally thin regions of the film. Surface

tension was thereby decreased at such thin spots, and the surface-tension gradients thus produced were in a direction causing the liquid to flow from the thinner into the thicker areas, thus promoting break-up of the film. The effect of surface-tension driven convection on the interfacial area of contact has also been discussed by Danckwerts et al. [D3] and Sawistowski [S3].

2.4 Summary

Most of the theoretical work undertaken thus far has dealt with the application of linear stability analysis to investigate the stability of models of physical systems subject to random infinitesimal perturbations. The models, in general, have been largely successful in the qualitative prediction of the occurrence of Marangoni instability, though quantitative agreement of the prediction of the precise conditions for the onset of Marangoni instability with the experimental results is unsatisfactory. Moreover, information about the growth of disturbances subsequent to initiation, or about the morphology of the fully-developed instability, cannot be obtained using linear stability analysis. Development of predictive mechanistic models for mass transfer in the presence of Marangoni instability has also been extremely limited.

Qualitative experimental studies have been carried out with a view to establishing the general morphology of the convective flows, and to obtain qualitative confirmation of the predictions of linear stability theory. Detailed information of the effect on the scale and intensity of the cellular convective flow of such variables as solute concentration, depth of the liquid layer, and relevant physico-chemical properties of the two phases has not been obtained. Practically no work has been carried out in flow systems.

Quantitative experimental work has dealt mainly with the determination of the enhancement of mass transfer in the presence of Marangoni convection. Most of the work has been carried out in simple systems having well-defined fluid mechanics in the undisturbed state. Data on systems and/or under conditions more closely representative of industrial practice are scarce, i.e. there exists practically no information on the manifestation of the Marangoni effect in gas-liquid systems where turbulence exists in the bulk of the liquid phase. Moreover, the effect of the relevant dimensionless groups, as determined by dimensional analysis, on the intensity of the Marangoni convection has not been established. It has been shown, however, that the occurrence of Marangoni instability can increase the rate of mass transfer several-fold, a result of some practical significance. An important finding was that Marangoni convection appeared to have a negligible effect on the gas-phase mass-transfer coefficient under the conditions studied.

CHAPTER THREE

DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTIONS INTO AIR IN A PACKED COLUMN

3.1 Introduction

Theoretical analyses predict that desorption from water into air of solutes which depress the surface tension should give rise to Marangoni instability provided that the driving force is sufficiently large for the Marangoni number to exceed its critical value. Brian *et al.* [B11] showed that desorption of solutes such as acetone, ether etc. from dilute aqueous solutions in a short wetted-wall column resulted in a substantial enhancement of the liquid-phase mass-transfer coefficient, a result of some practical significance. There is a great dearth of information, however, on the effect of convective instability on the gas- and liquid-phase mass-transfer coefficients in systems more representative, as regards regimes of flow, of those found in industrial practice. It should be noted that at present it is not possible to deduce from the results obtained under one set of hydrodynamic conditions the influence of Marangoni convection, if any, under a completely different set of hydrodynamic conditions, even for the same absorption system.

Experiments were therefore performed with a view to determining the effect of convective instability, induced by the desorption of solutes which depress the surface tension, on the rate of mass transfer in a small packed column. Acetone was desorbed from dilute aqueous solutions to promote Marangoni instability. Carbon dioxide was simultaneously desorbed to monitor the value of the liquid-phase mass-transfer coefficient, the desorption of CO_2 being essentially liquid-film controlled. It should be noted that the transfer of acetone is largely

controlled by the resistance in the gas film.

Idealised laboratory contactors are often used as small-scale models for predicting the behaviour of industrial contactors [A2,D2], and data obtained therein used for the design of industrial equipment. However, mass transfer data obtained in the presence of the Marangoni effect in such idealised contactors cannot, in general, be extrapolated to systems with entirely different hydrodynamic conditions. The comparison of data obtained in the presence of the Marangoni effect in the packed column with those obtained in the short wetted-wall column, for the same absorption system, should throw some light on the uncertainties involved in the extrapolation of data to widely different hydrodynamic conditions.

3.2 Experimental Apparatus and Procedure

The packed column was made of glass and had an inside diameter of 5.1 cm. The overall height of the column was 60 cm. Approximately two-thirds of the available column height was filled with the packing. The packing was supported by means of a simple perforated base-plate. Air in countercurrent flow to the liquid was introduced by means of three symmetrically placed 8 mm diameter tubes situated on the circumference of the packed column. Four sets of such tubes, spaced 10 cm apart along the height of the column,were provided in order to vary the height of the exposed packing if required. The liquid level in the column could be maintained just below the gas inlet tubes by means of an external constant-level device. The liquid was introduced by means of a simple distributor which consisted of a central glass tube terminating in four 4 mm diameter discharge nozzles symmetrically arranged on a pitch circle diameter of 2 cm. The liquid distributor was lowered to within 5 mm of

the top of the packing to avoid any splashing. The liquid distribution obtained was satisfactory for the purposes of the experiment.

The column was packed with ceramic Raschig rings; two sizes of rings, 0.64 cm and 0.95 cm, were used. The wall thickness for the 0.64 cm rings was 0.08 cm and the packing density was approximately 3.27 rings per cm^3 of packing. The wall thickness for the 0.95 cm rings was 0.16 cm and the packing density was approximately 0.9 rings per cm^3.

For most of the experiments, the inlet liquid contained dissolved acetone (0 - 1.2 wt. %) and carbon dioxide (approximately in the range 40 - 70% of its saturation value). Both these solutes were simultaneously desorbed in the column. In order to maintain a high driving force for the desorption of acetone and thus obtain relatively vigorous convection due to the Marangoni effect, as well as to keep the concentration changes in the liquid to a minimum, short heights of exposed packing were used, 5.5 cm for the 0.95 cm rings, and 10 cm for the 0.64 cm rings. The liquid was stored in a glass reservoir of 50 litres capacity kept at a height of approximately 4 metres relative to the top of the packed column. This ensured that the change in the liquid-head was negligible during the course of a run. The liquid in the feed reservoir contained dissolved CO_2. Acetone was introduced into the liquid stream by means of a continuously variable and accurately calibrated electronic peristaltic micropump. The acetone was stored in a separate one-litre glass vessel which was connected by means of flexible tubing to the peristaltic pump and a glass burette. The burette was used to make frequent checks on the calibration of the peristaltic pump. Silicone rubber tubing was used for conveying pure acetone and was found to be satisfactory. Before using any piece of silicone tubing, acetone was pumped through the tubing for several days to flush out any soluble impurities. Ordinary

flexible poly-vinyl-chloride tubing was used for all other liquid lines and was found to be satisfactory.

The inlet liquid flow rate was measured by means of a calibrated rotameter, and controlled by means of a stainless-steel needle valve. Air from a central compressor was passed through a high-efficiency oil-mist filter and then through a heating coil immersed in a water bath maintained at approximately 25°C. It was then saturated with water vapour by bubbling it through water in a glass vessel which was also immersed in a thermostated bath kept at approximately 25°C. The inlet gas flow rate was measured by means of a calibrated rotameter and controlled by means of a needle valve. Before passing the air through the oil filter, the pressure was reduced to the required value by means of a pressure reducer. The outlet liquid from the column was led directly to the drain and the outlet gas was exhausted into the gas vent. Liquid was not reused because even small changes in the level of accidental contamination could substantially affect the Marangoni convection. For this reason, it was also ensured that the solutions used had the same "history" prior to use. Once-distilled water, obtained from the same source, was used for all the experiments, and was stored before use in thoroughly cleaned polypropylene carboys. All necessary pumping was done by means of a peristaltic pump to avoid contamination. Suitable sampling points were incorporated for removing samples of the inlet and outlet liquid for analysis, as well as for sampling a bleed from the outlet gas. The inlet and outlet liquid samples were analysed to determine the concentration of dissolved carbon dioxide. The bleed from the outlet gas stream was passed through a series of bubblers containing distilled water for a pre-determined length of time, and the outlet acetone concentration in the gas leaving the column was determined by determining the amount of acetone absorbed in the scrubbing bottles.

The flow rate of the bleed stream was measured by means of a calibrated rotameter. Standard techniques were used to determine the concentration of dissolved CO_2 and acetone in aqueous solutions and are described in Appendix 1. Samples were taken after the system had reached steady state, the time required having been determined in preliminary experiments and being of the order of approximately 10 to 15 minutes.

Under the experimental conditions, the CO_2 concentration in the exit gas phase was small enough to be neglected. The values of the liquid-phase mass-transfer coefficient, $k_L\underline{a}$, were computed from the CO_2 concentration in the inlet and outlet liquid streams assuming that the liquid was essentially in plug flow. It should be noted that for the desorption of CO_2, the mass-transfer resistance in the gas phase was negligible. In the case of acetone desorption, however, roughly eighty per cent of the resistance to mass transfer was in the gas phase. The values of the overall gas-phase mass-transfer coefficient, $K_G\underline{a}$, were calculated from a knowledge of the concentration of acetone in the inlet liquid stream and in the outlet gas stream. An arithmetic average driving force was used. The values of the gas-side mass-transfer coefficients were calculated from the overall values by correcting for the liquid-side resistance using the simple additivity of resistances concept [B11]. Since the liquid-side resistance was generally small, the correction could be made without significant error. For the 0.95 cm packing, $k_G\underline{a}$ data (as well as $\underline{a}$ data) are available in the literature [V3]. The change in the concentration of acetone in the liquid was found to be negligible.

The entire apparatus was assembled in a constant-temperature room which was maintained at 25 ± 1°C. The total pressure in the system was essentially atmospheric. Thermometers were placed in the inlet and

outlet liquid lines and in the inlet gas line to monitor the temperatures of the respective streams, and to check that the inlet fluid streams were essentially at room temperature. The temperature change of the liquid was found to be negligible.

Some experiments were carried out to measure the rate of absorption of pure, humidified and virtually stagnant CO_2 into distilled water free from dissolved CO_2. In these experiments the gas exit was closed, and the rate of absorption determined by measuring the rate at which CO_2 entered the absorption column. Humidified CO_2 was stored in a rubber balloon kept in an unstretched condition to maintain the gas inside the system at practically atmospheric pressure, and the rate of absorption was measured by means of a soap-film meter. In these experiments, the distilled water used was thoroughly deaerated by spraying the water into the liquid reservoir kept under high vacuum. Details of this method, sometimes referred to as the "uptake" method, are to be found in the literature [D2,S6].

The CO_2 used in the experiments was obtained from high-pressure cylinders and was of high purity (greater than 99.9%). The acetone used was AR grade. Because of the low concentrations of acetone and CO_2 in the distilled water, the two solutes were assumed to diffuse independently of each other. Furthermore, the physical properties of the solution were practically the same as those of pure water. The relevant physico-chemical properties of the solutes employed are given in Appendix 1.

Before the apparatus was assembled, all the component parts were thoroughly cleaned, and during assembly and subsequent use due care was exercised to avoid any contamination by grease or extraneous surface-active agents.

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Before the apparatus was assembled, all the component parts were thoroughly cleaned, and during assembly and subsequent use due care was exercised to avoid any contamination by grease or extraneous surface-active agents.

To execute a run, the gas and liquid flow rates were adjusted to the desired values. The temperatures of the inlet and exit lines were noted, and it was checked that the entering liquid and gas phases were at essentially 25°C. The micropump for feeding acetone was started and adjusted to give the desired flow rate. After the steady state had been reached, samples were taken of the inlet and outlet liquid. To measure the concentration of acetone in the outlet gas phase, a bleed from the exit gas was bubbled through water kept in a series of bubblers for a predetermined length of time, and the acetone concentration in the liquid determined subsequently. To generate the bleed stream, the end of the line was connected to a source of constant vacuum. The flow rate of the bleed stream could be adjusted by means of needle valves situated beyond the series of bubblers. The experimental set-up is shown schematically in Figure 3-1.

In this work the liquid superficial velocity, v_L, was varied in the range 0.18 cm/s to 0.6 cm/s. The gas superficial velocity, v_G, was varied from around 10 cm/s to 27 cm/s. For a large majority of the experiments, the gas superficial velocity was 20 cm/s. After completing a set of experiments, the apparatus was thoroughly flushed with freshly distilled water.

3.3 Results and Discussion

The effect of the liquid flow rate on the values of the liquid-phase mass-transfer coefficient (as determined from the rates of desorption of CO_2) in the absence of the Marangoni effect, $(k_L\underline{a})^*$, is shown in Figure 3-2. The asterisk will henceforth be used to indicate values of dependent variables in the absence of the Marangoni effect. The values obtained by absorption of pure CO_2 by the uptake method are seen to be in excellent agreement with those obtained from the rate of

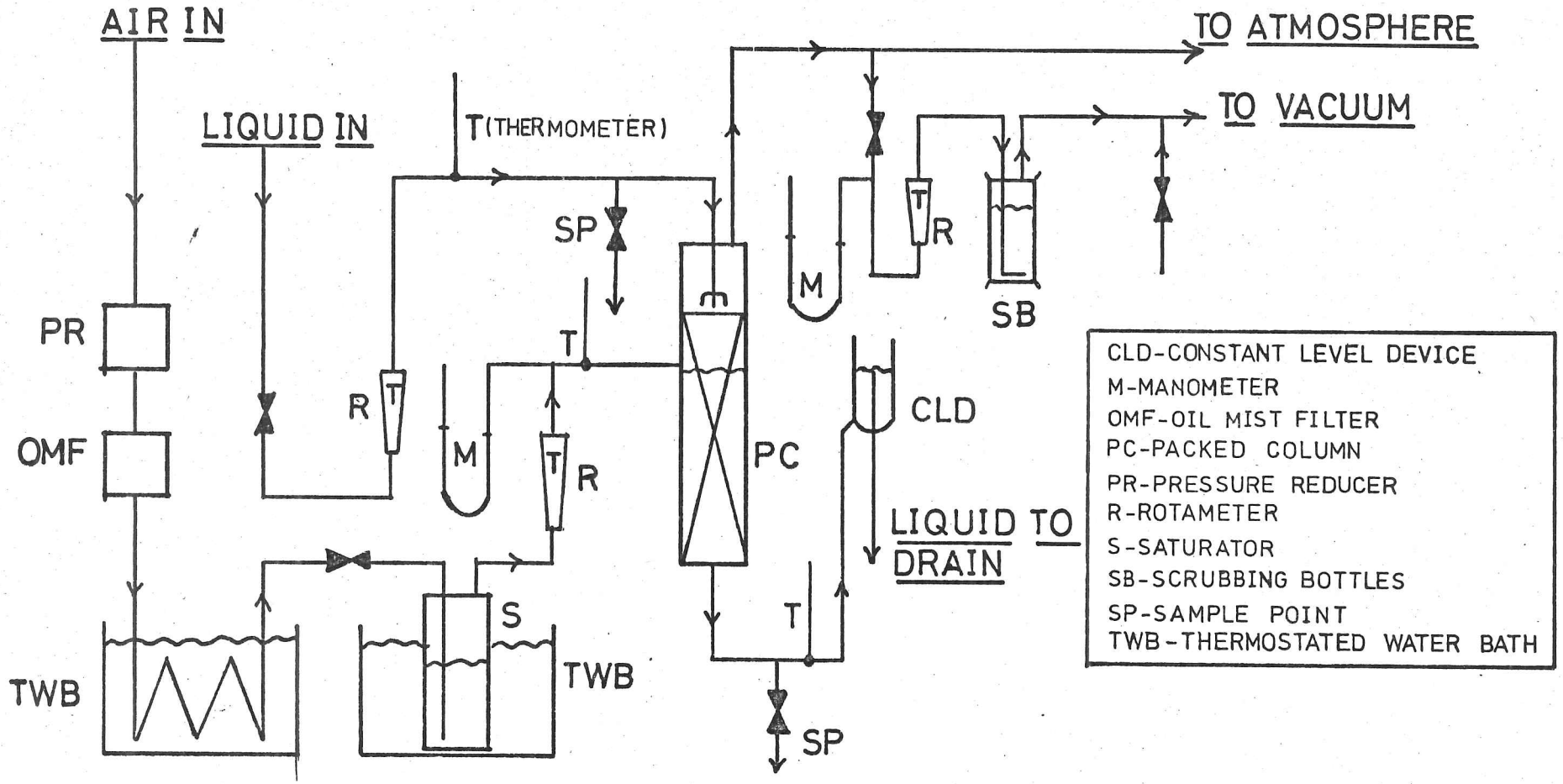

FIG.3-1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET-UP FOR THE PACKED COLUMN

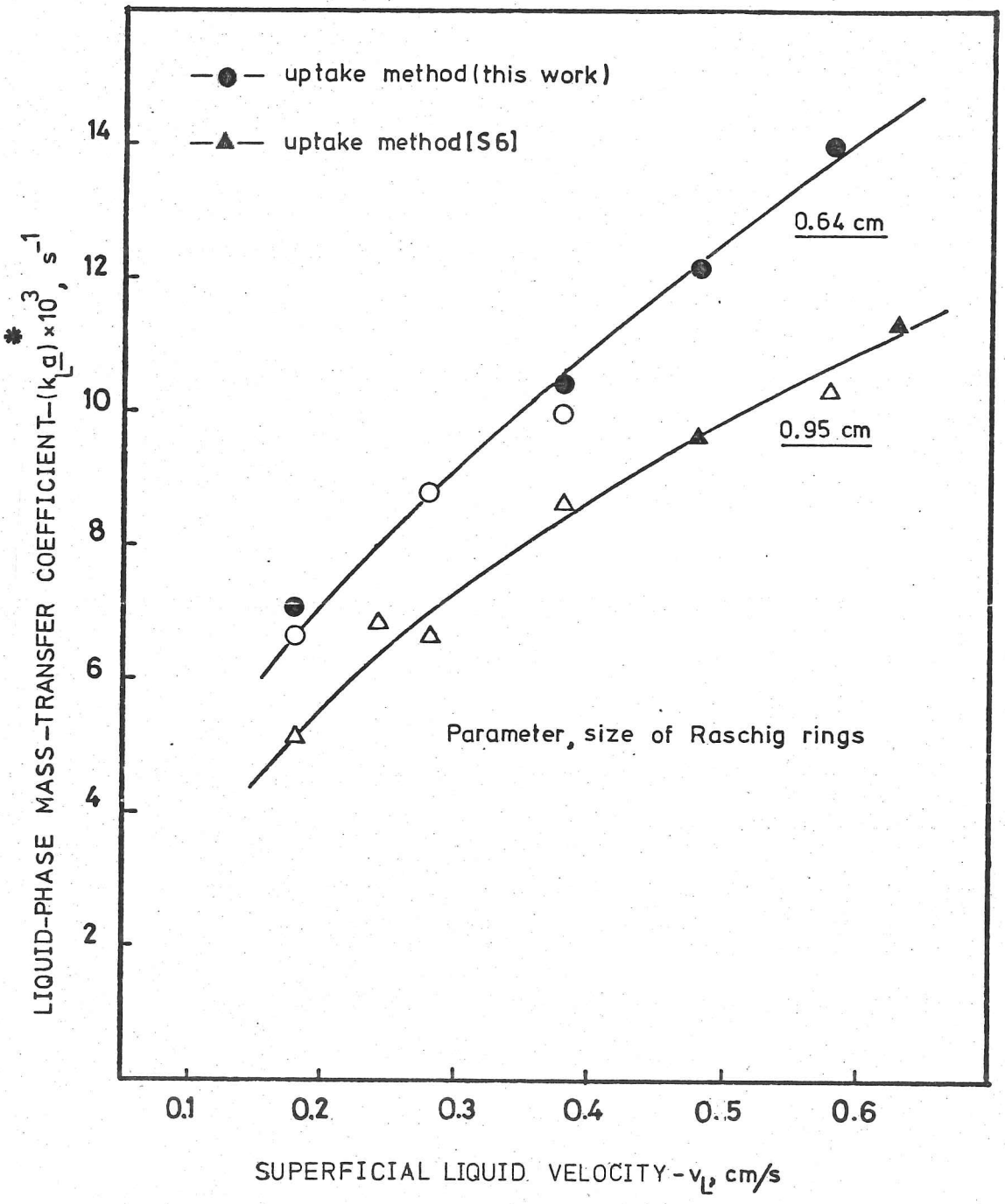

FIG. 3-2 DESORPTION OF CO_2 FROM WATER INTO AIR IN THE PACKED COLUMN ; 25°C, 1 atm

desorption of CO_2 into air. It can therefore be concluded that the method of gas introduction did not introduce any measurable end-effect with regard to transfer in the liquid phase. Moreover, the agreement substantiates the accuracy of the chemical analysis used for measuring the concentration of dissolved CO_2 in water. For the 0.95 cm Raschig rings, the data of Sharma [S6] are also plotted and are seen to be in very good agreement with the data obtained in this work.

The effect of acetone desorption on the liquid mass-transfer coefficient is shown in Figures 3-3 and 3-4 for the 0.64 cm and 0.95 cm packing, respectively. It can be seen that desorption of acetone in general results in a significant increase in the value of the liquid-phase mass-transfer coefficient. The plots further show that at fixed liquid- and gas-phase flow velocities, an increase in the concentration of acetone in the liquid feed results in an increase in the value of $k_L a$. This enhancement is attributed to Marangoni convection driven by surface-tension gradients induced by the desorption of acetone. The strong dependence of the mass-transfer coefficient on the concentration of the solute is a characteristic feature of the occurrence of Marangoni convection. It is concluded that in the range investigated, an increase in the concentration of acetone results in an increase in the intracellular surface-tension gradients leading to more vigorous convective motion and hence a higher rate of surface renewal.

The effect of the liquid flow rate on the liquid-phase enhancement factor, E_L, is shown in Figure 3-5 for the 0.95 cm packing. The plot shows that for a given acetone concentration in the liquid feed, an increase in the liquid superficial velocity leads to a decrease in the value of E_L. In a packed column, an increase in the liquid superficial velocity increases the rate of surface renewal or rejuvenation [D2] in

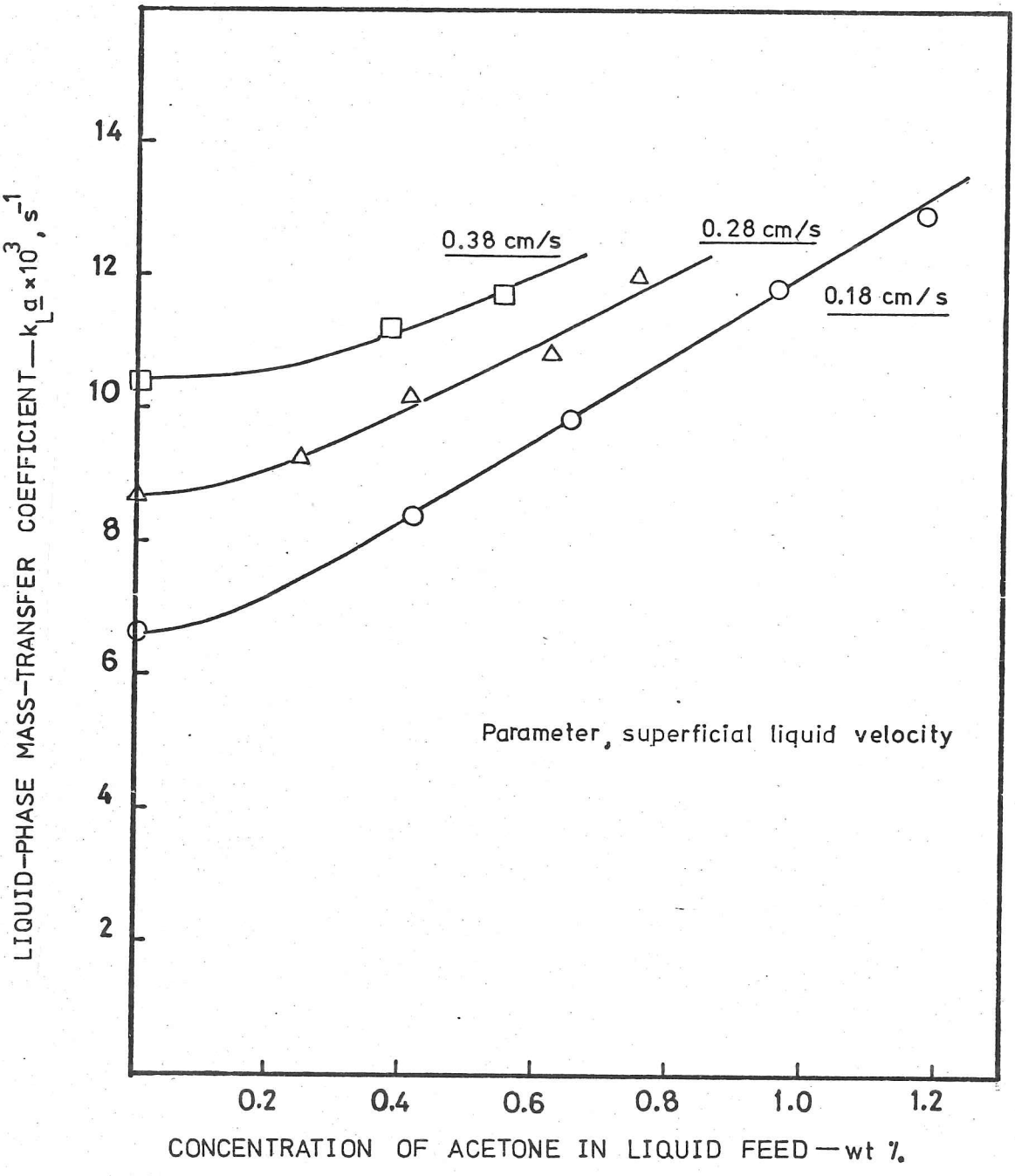

FIG. 3-3 DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE — PACKED COLUMN ; 0.64 cm RASCHIG RINGS; v_G=20 cm/s ; 25° C, 1 atm

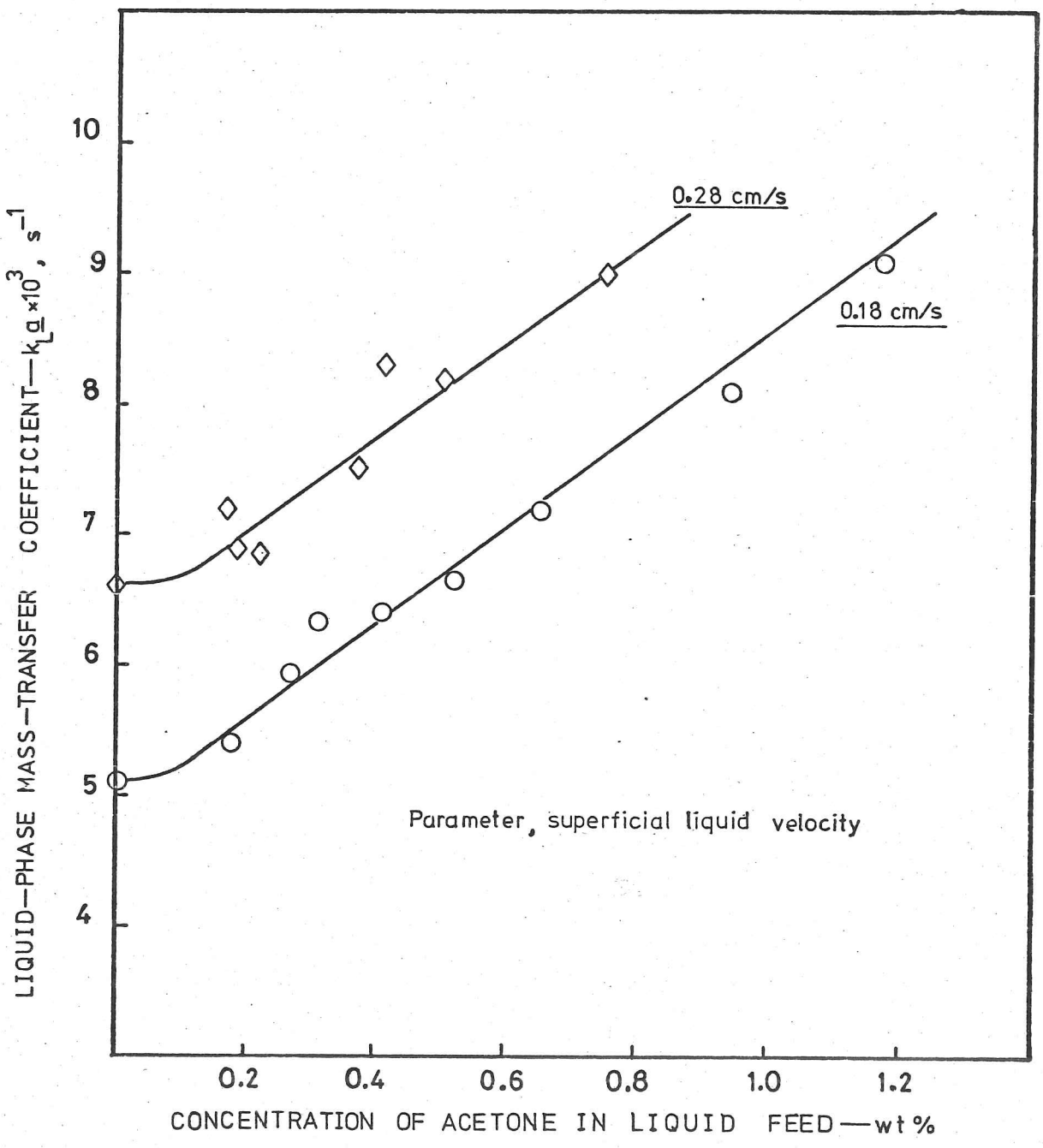

FIG. 3-4 DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE — PACKED COLUMN; 0.95 cm RASCHIG RINGS; v_G=20 cm/s; 25°C, 1 atm

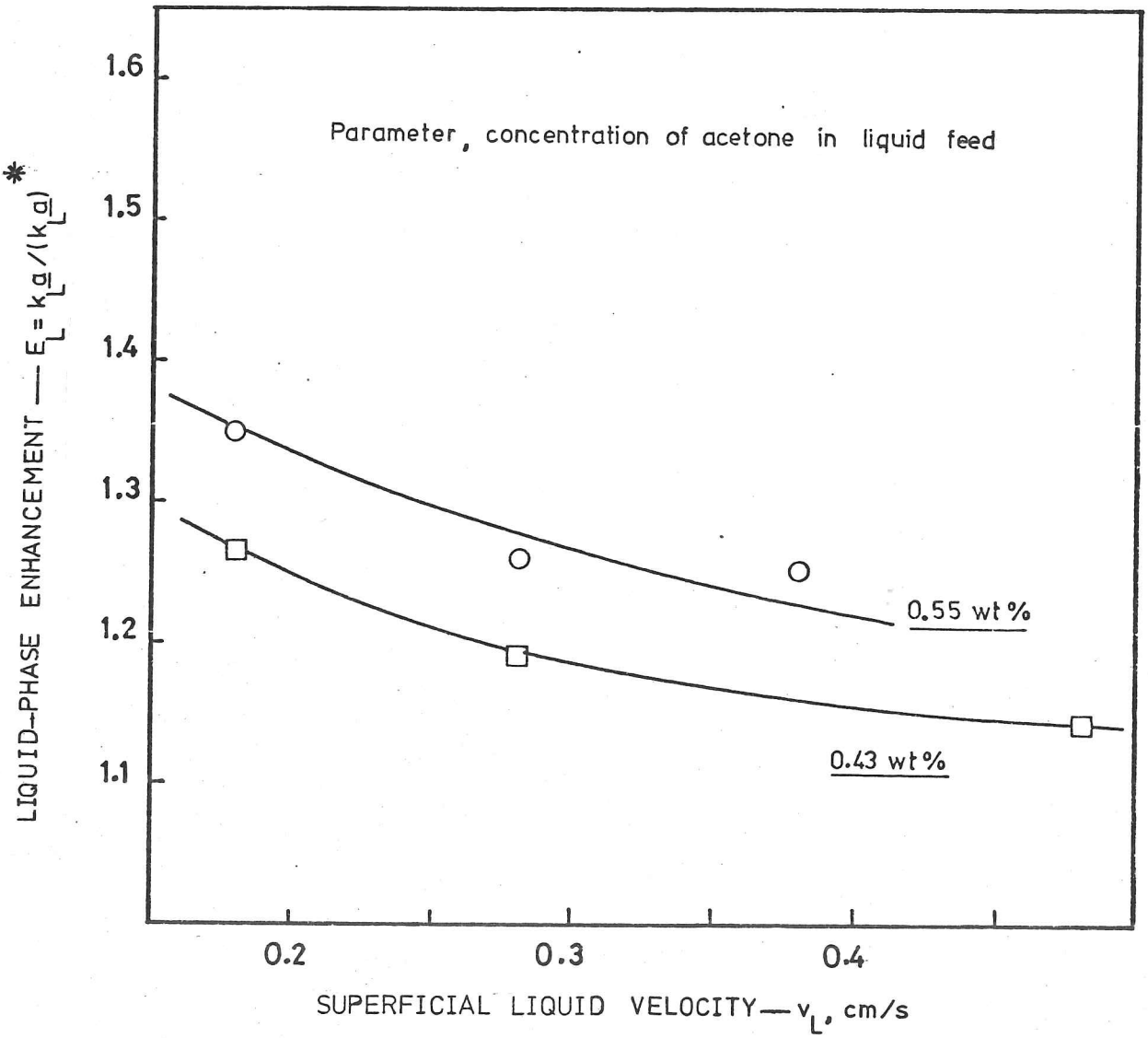

FIG. 3-5 EFFECT OF LIQUID FLOW RATE ON THE LIQUID-PHASE ENHANCEMENT FACTOR — PACKED COLUMN ; 0.95 cm RASCHIG RINGS ; $v_G = 20$ cm/s

the unperturbed state. Surface rejuvenation is said to occur when the eddies of fluid from the bulk approach very close to the surface but do not actually result in localised renewal of the surface. In the context of this thesis, however, the term surface-renewal will be used in a general sense, and will be assumed to incorporate the process of surface rejuvenation where relevant. If, therefore, the reinforcement in the rate of surface renewal due to the Marangoni effect is largely independent of the liquid flow rate, an increase in v_L would result in a decrease in the value of E_L, other things being equal. In the present experiments the interpretation of the results is further complicated by the fact that an increase in the liquid superficial velocity increases the effective interfacial area of contact, $\underline{a}$. For a fixed gas superficial velocity, this results in a decrease in the effective overall driving force for acetone desorption, which in turn would be expected to lead to a decrease in the value of E_L. However, because of the short height of packing employed, the maximum change in the overall driving force was calculated to be only 4 per cent for the 0.95 cm packing. An examination of Figure 3-3 reveals a similar effect of v_L on E_L for the 0.64 cm packing. In this case, however, the effect of the decrease in the overall driving force is significant as evidenced by the relatively sharper fall in the value of E_L with increasing liquid superficial velocity, other things remaining equal. In the extrapolation of data showing the effect of liquid flow rate on E_L, due care must be exercised to ensure that the extrapolation is not extended to regions where the hydrodynamic regime of the flowing liquid in the unperturbed state is radically altered.

Because of the low concentration of acetone in the liquid, the change in the "wetting properties", as a result of the change in the surface tension, of the aqueous solutions relative to pure water was expected to be insignificant. In other words, the interfacial area of contact was

assumed to be independent of the concentration of acetone in the range studied. This was verified by absorbing carbon dioxide into aqueous solutions of acetone under conditions whereby there was no net transfer of acetone. This was achieved by ensuring that the partial pressure of acetone in the inlet gas was at equilibrium with respect to the concentration of acetone in the inlet liquid. A low gas superficial velocity was employed (0.75 cm/s), and the gas was humidified and saturated with acetone by bubbling it through a large glass vessel containing aqueous acetone at the same concentration as the inlet liquid. The capacity of the vessel was such that the change in the concentration of acetone was insignificant during the course of a run. The vessel was kept in a thermostatic bath maintained at 25°C, and the low gas flow rate ensured that the acetone in the gas leaving the saturator was essentially at equilibrium with the concentration of acetone in the liquid in the vessel. The vessel was refilled with fresh solution of the appropriate concentration after every run. The experimental results for the 0.95 cm packing are plotted in Figure 3-6 and show that the values of $k_L\underline{a}$ obtained were practically independent of the acetone concentration in the inlet liquid and equal to those for pure water, under conditions of zero acetone flux, for a liquid superficial velocity of 0.18 cm/s.

The effect of Marangoni convection on the gas-phase mass-transfer coefficient is shown in Figure 3-7. The plot shows the effect of the concentration of acetone in the liquid on the values of $k_G\underline{a}$. It is seen that desorption of acetone has virtually no effect on the mass transfer in the gas phase under the conditions studied. The values of $k_G\underline{a}$ were obtained by measuring the rate of acetone desorption and correcting for the resistance in the liquid phase. It was assumed that the liquid-phase mass-transfer coefficient is proportional to the square root of the solute diffusivity. The result is in agreement with the conclusions of previous

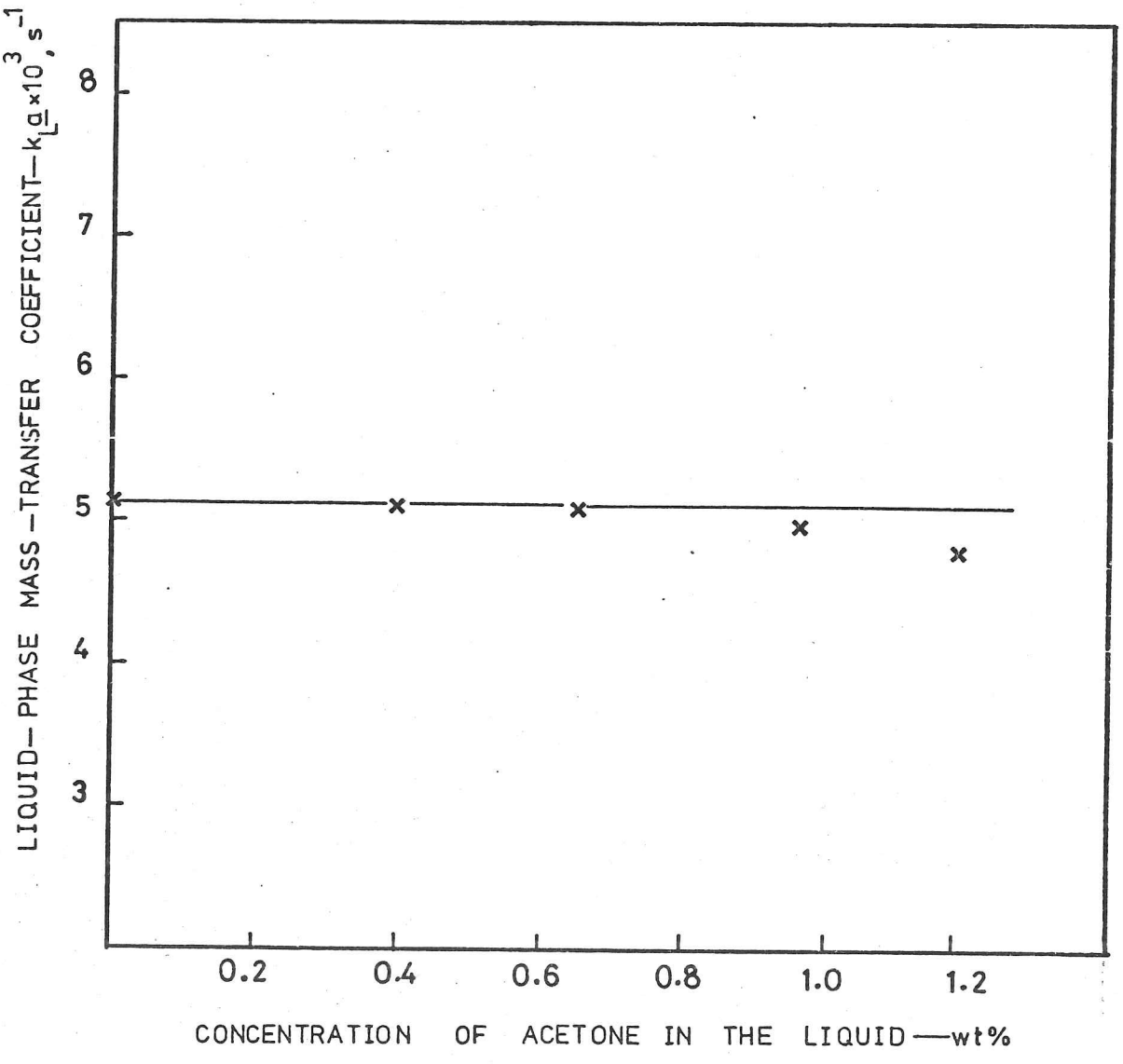

FIG.3-6 ABSORPTION OF CO_2 INTO DILUTE AQUEOUS SOLUTIONS OF ACETONE UNDER CONDITIONS OF ZERO NET FLUX OF ACETONE — PACKED COLUMN; 0.95 cm RASCHIG RINGS; v_L = 0.18 cm/s, v_G = 0.75 cm/s; 25° C, 1 atm

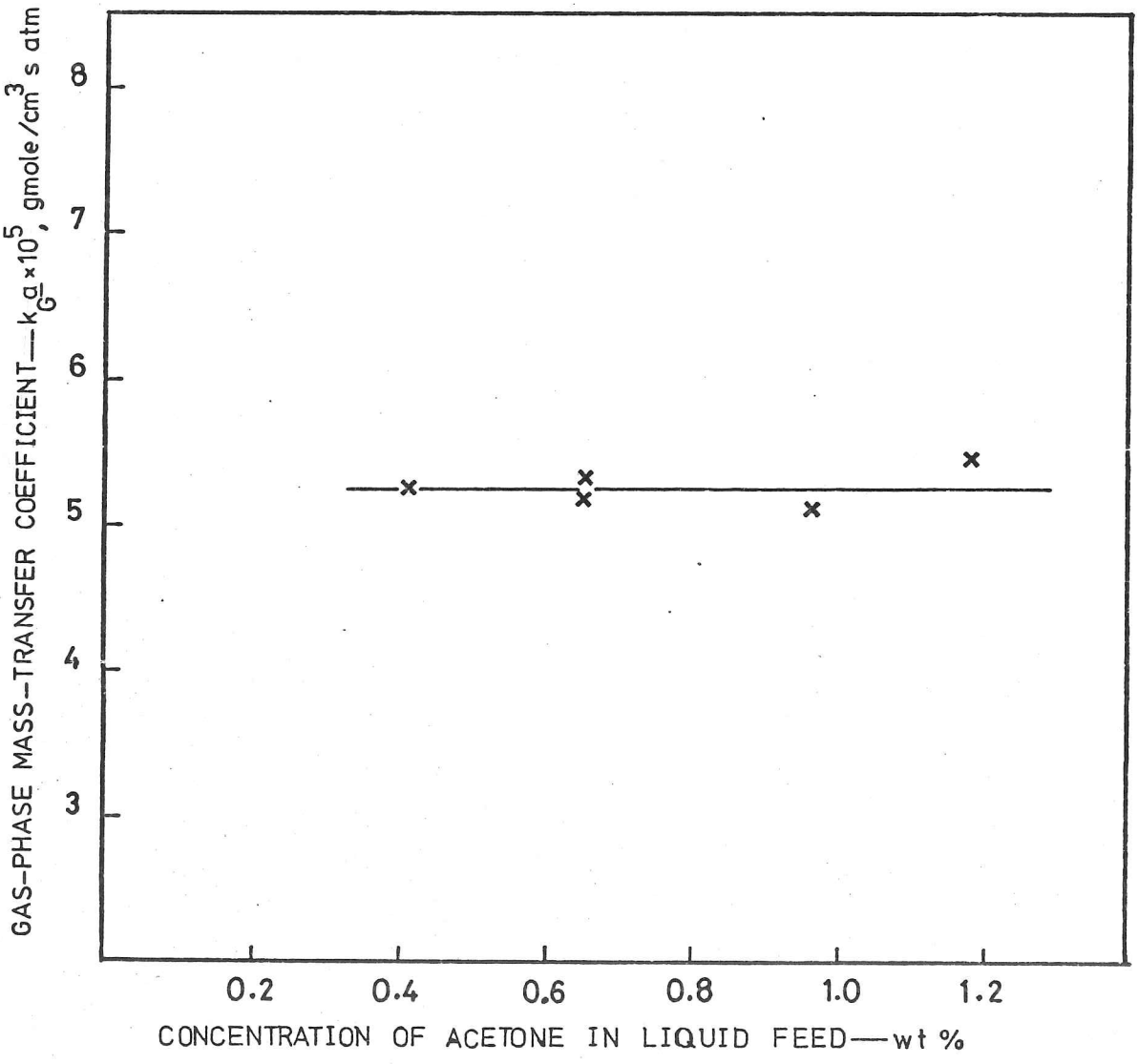

FIG.3-7 DESORPTION OF ACETONE FROM WATER INTO AIR — PACKED COLUMN; 0.64 cm RASCHIG RINGS; $v_L = 0.18$ cm/s, $v_G = 20$ cm/s ; 25°C, 1atm

workers [B11,C1] who reported similar observations in simple laboratory contactors, and appears to have general validity. It seems that the scale and/or the intensity of the Marangoni convection in the gas phase is not large enough to influence the mass transfer in the gas phase where the value of the Schmidt number is relatively very small. Because of the relatively large values of diffusivity in the gas phase, the gas-phase concentration boundary layer is orders of magnitude thicker than the concentration boundary layer in the liquid phase. The results reinforce the conclusion that the effective interfacial area remains essentially independent of acetone concentration in the liquid. It should be noted that reduction in interfacial area due to break-up of the film into rivulets during acetone desorption is highly unlikely. Desorption of solutes which depress the surface tension in fact stabilises the liquid film according to the currently accepted mechanism of rupture of flowing liquid films [B5].

The effect of the superficial velocity of the gas on the liquid-phase enhancement is shown in Figures 3-8 and 3-9 for the 0.64 cm and 0.95 cm packing, respectively. The plots show that an increase in the gas superficial velocity, and hence in the value of k_G, results in a substantial increase (around 40 per cent in the range studied) in the liquid-phase enhancement, E_L, indicating an increase in the intensity of the convective motion due to the Marangoni effect. It is well established that in packed columns, in the absence of Marangoni instability, the gas velocity has no effect on the mass transfer in the liquid phase upto the loading point. In the case of desorption of acetone, since the major resistance to transfer is in the gas phase, an increase in k_G results in an increase in the rate of desorption. This ultimately results in larger effective surface-tension gradients and, hence, more vigorous interfacial convection. The increase in the overall driving

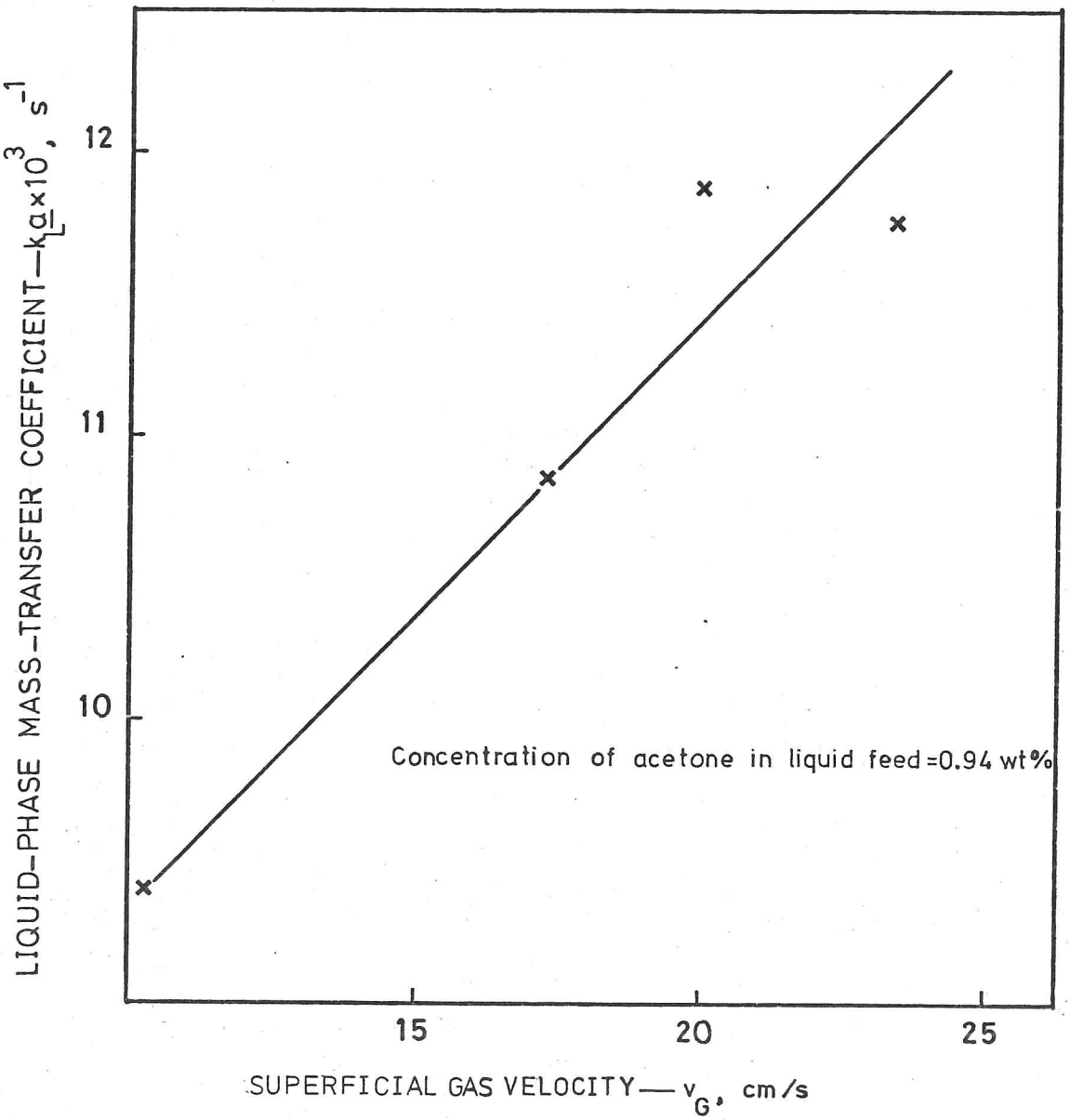

FIG. 3-8 EFFECT OF GAS FLOW RATE ON THE DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE—PACKED COLUMN; 0.64 cm RASCHIG RINGS; v_L=0.18 cm/s; 25° C, 1 atm

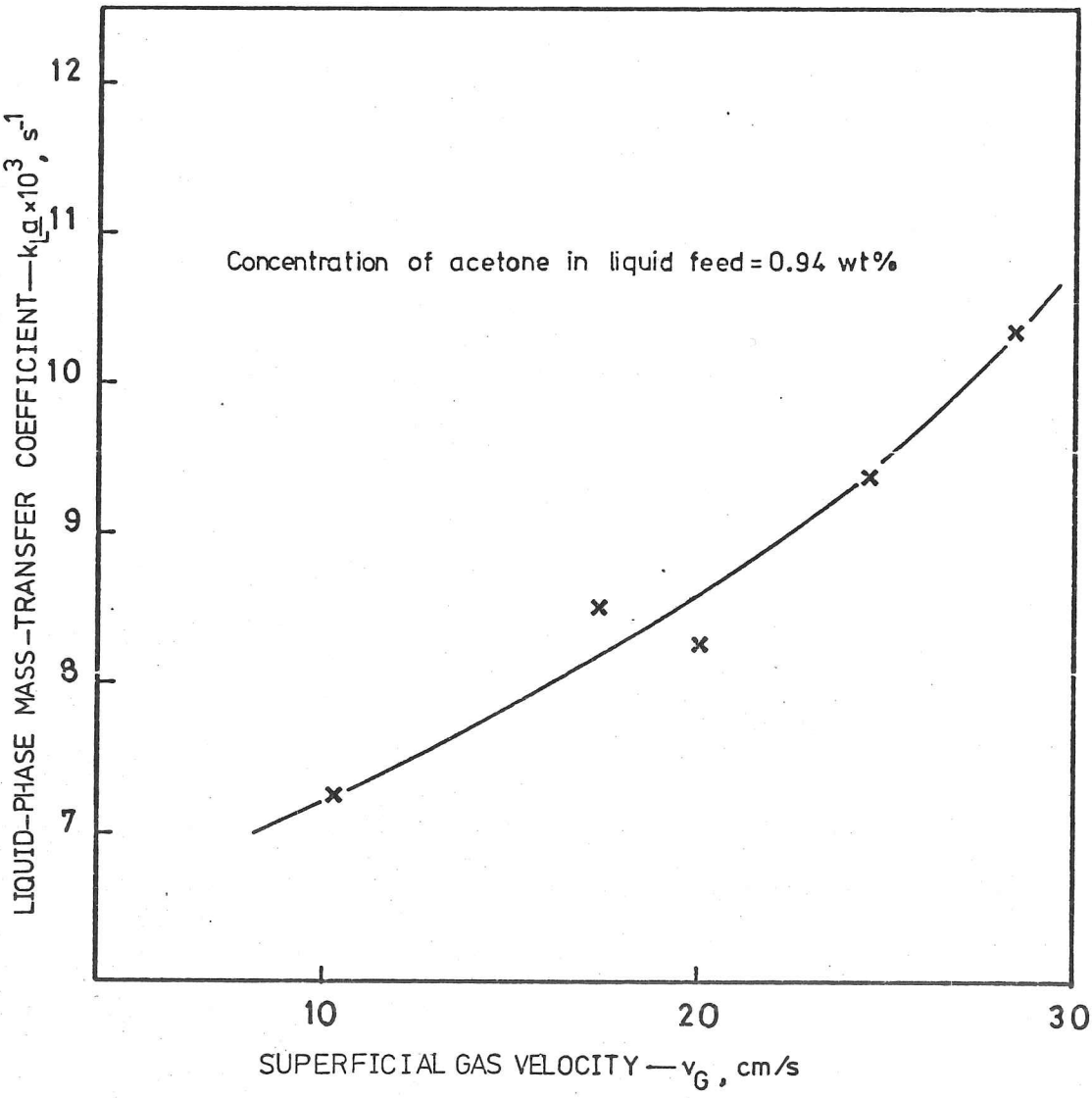

FIG.3-9 EFFECT OF GAS FLOW RATE ON THE DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE—PACKED COLUMN ; 0.95 cm RASCHIG RINGS ; v_L = 0.18 cm/s ; 25°C, 1 atm

force due to an increase in the gas flow rate was of little significance.

It is speculated that the behaviour described above is only one aspect of the overall response of a system susceptible to Marangoni disturbances, induced by desorption of solutes which depress the surface tension, to a change in the value of k_G. Dimensional analysis shows that the relevant dimensionless groups can be arranged in such a way that the only dimensionless group containing k_G is (Hk_G^*/k_L^*), i.e. the ratio of the resistance to transfer in the liquid phase to that in the gas phase in the absence of convective instability [see Appendix 2]. Consider for the sake of analysis a gas-liquid system wherein the liquid- and gas-phase hydrodynamics are specified, in the absence of Marangoni convection, by the values of k_L^* and k_G^*. Since the gas-phase mass-transfer coefficient appears in general to be essentially unchanged by the occurrence of Marangoni convection, the asterisk associated with k_G will be dropped. For the sake of clarity all other dimensionless groups will be assumed to be held constant. Since k_L^* appears in several of these groups, the analysis is thus restricted to constant k_L^*, and hence any variation in the resistance ratio, R_r, is due solely to a change in the value of k_G for a given solute. It is also assumed that the value of k_G can be changed without any change in k_L^*. In what follows, some speculations are made about the possible effect of k_G on the enhancement of the liquid-phase mass-transfer coefficient in the case of Marangoni convection induced by the desorption of solutes which lower the surface tension.

For very small values of R_r, the concentration of acetone should be essentially uniform throughout the liquid phase and the concentration gradients established correspondingly small. If the concentration gradients are sufficiently large, convective instability will occur. However, for very small values of R_r the effective intracellular gradient of

surface tension would be small, and the ensuing motion would be expected to be weak. The liquid-phase enhancement factor would therefore be very nearly equal to unity. An increase in the value of k_G would lead to relatively more rapid removal of solute resulting in relatively larger effective intracellular gradients of surface tension and correspondingly more vigorous convective flow.

For sufficiently large values of k_G, due to the extremely rapid removal of solute from the surface, the concentration of solute everywhere at the surface would be practically zero and hence essentially uniform. Fresh elements of liquid on reaching the surface from the bulk of the liquid would have their surface concentration reduced virtually instantaneously to zero and hence gradients of surface tension cannot exist. In the event that k_G is not large enough to reduce the surface concentration instantaneously to zero, it is possible for convective instability to manifest itself. However, for moderately large values of k_G, the rapid removal of the solute from the surface will result in relatively weak effective intracellular surface-tension gradients. In such cases, an increase in the value of k_G will promote stability by tending to eliminate the occurrence of surface tension gradients. In the case of quiescent gas-liquid systems, Brian and Ross [B14] have shown theoretically that as R_r tends towards infinity, the critical Marangoni number increases without limit.

Hence, in general, it appears that a plot of E_L versus R_r should exhibit a maximum at some value of R_r, and that E_L should tend towards unity for sufficiently small as well as sufficiently large values of R_r. A change in the values of the other dimensionless groups would change only the position of the curve, retaining the basic shape.

It is unlikely, under the conditions generally encountered in

practice, for the entire range of behaviour postulated above to be demonstrated for any one solute. However, different solutes with widely varying values of the Henry's law constant, H, would be in different regions of the overall curve in a given apparatus, and the system could respond differently to a change in the value of k_G for each of the different solutes.

It should be emphasised that the arguments employed above are extremely general in content. For example, no attempt has been made to distinguish between the occurrence of Marangoni convection in turbulent and quasi-quiescent systems e.g. laminar jets, falling liquid films etc. In addition, detailed discussion of the effect of k_G on the morphology and the rate of growth of Marangoni instability has not been attempted, and the complicating effect of the Gibbs adsorption layer has been neglected. However, it appears on the basis of the currently available, albeit scanty, information that the essential features of the E_L versus R_r plot would apply equally to turbulent as well as non-turbulent systems.

No attempts have been made by previous investigators to study in detail the occurrence of the Marangoni effect in inherently turbulent systems. It should be noted that for turbulent systems in general interfacial convection, and hence surface renewal, occurs even in the absence of Marangoni disturbances. In such systems, surface tension gradients can arise due to bulk liquid being brought up to, or close to, the surface by the action of turbulent eddies as well as due to the growth of random infinitesimal disturbances. The characteristics of the turbulent flow, in addition, would be expected to have a bearing on the morphology of the interfacial convection caused by surface-tension inhomogeneity.

The effect of the gas and liquid flow rates on the values of $k_G a$

for the 0.64 cm packing is shown in Figures 3-10 and 3-11. In packed columns, the liquid flow rate has essentially no effect on k_G, and hence the increase in $k_G\underline{a}$ as a result of an increase in the liquid flow rate can be attributed to an increase in the value of $\underline{a}$. Furthermore, in packed columns the gas superficial velocity has virtually no effect on the effective interfacial area upto the loading point.

Figures 3-3 and 3-4 appear to indicate the existence of a minimum non-zero value of the acetone concentration in the liquid for the onset of Marangoni convection. In order to examine this point further, a plot was made for the 0.95 cm packing of the logarithm of the liquid-phase enhancement, E_L, against the logarithm of a modified Marangoni number (Figure 3-12). The definition of the Marangoni number was the same as that employed by Brian et al. [B11,M2], viz. the ratio of the product of the average driving force for acetone desorption in the liquid phase and the absolute value of the concentration coefficient of surface tension to the product of the liquid-phase mass-transfer coefficient in the unperturbed state, k_L^*, and the viscosity of the liquid phase. The figure appears to indicate the existence of a critical Marangoni number, which is obtained from the plot by means of a small extrapolation to E_L equals unity. The "experimental" critical Marangoni number thus obtained is roughly an order of magnitude larger than that obtained for the same system in a short wetted-wall column by Brian et al. [B11]. The reasons for this are not entirely clear, though as pointed out earlier the presence of minute traces of contaminants can drastically alter the conditions for the onset of Marangoni convection. The important point to note, however, is that there appears to be a critical Marangoni number for the system irrespective of absolute magnitude.

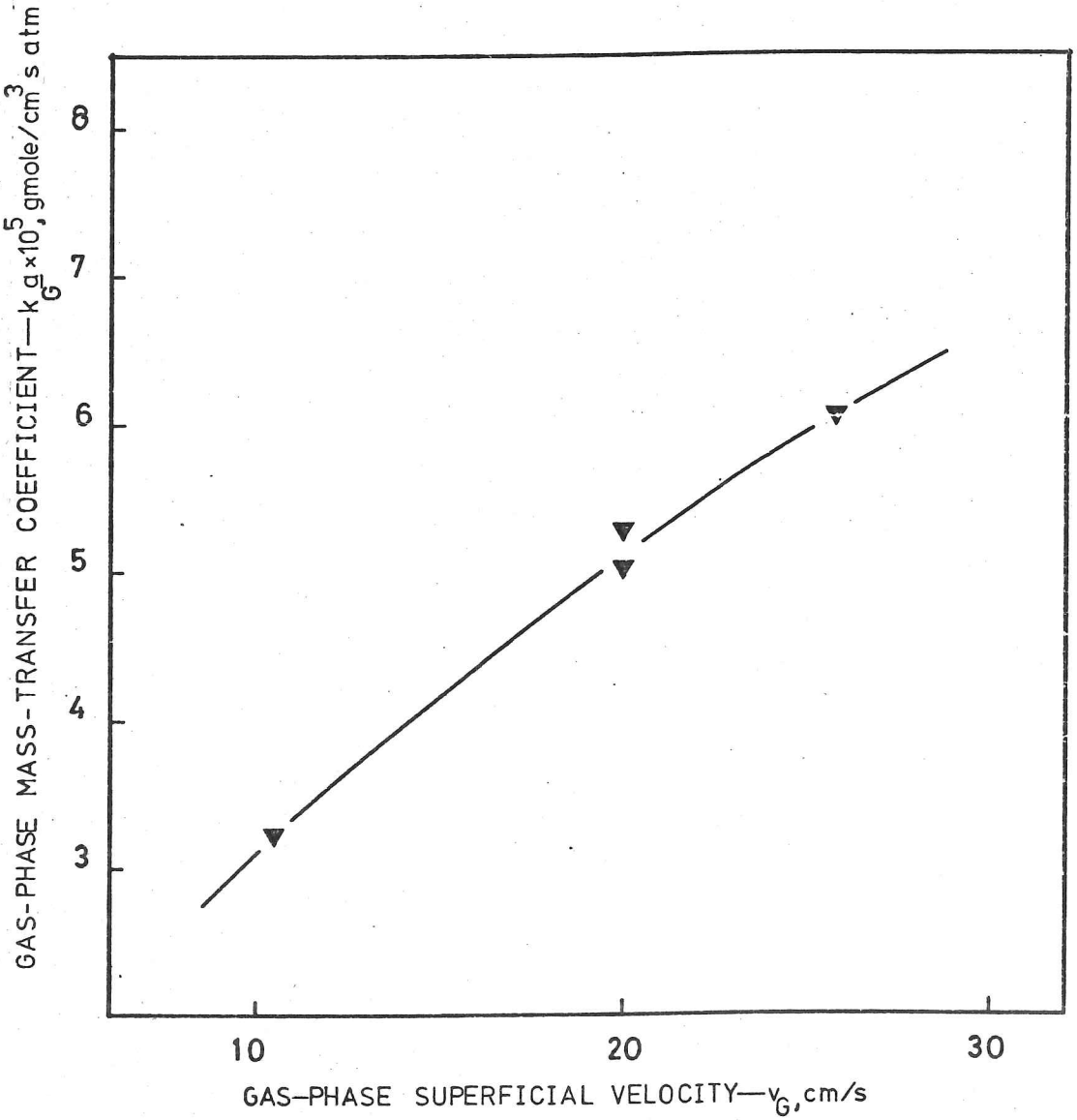

FIG. 3-10 DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTIONS INTO AIR — PACKED COLUMN; 0.64 cm RASCHIG RINGS; v_L = 0.18 cm/s; 25°C, 1 atm

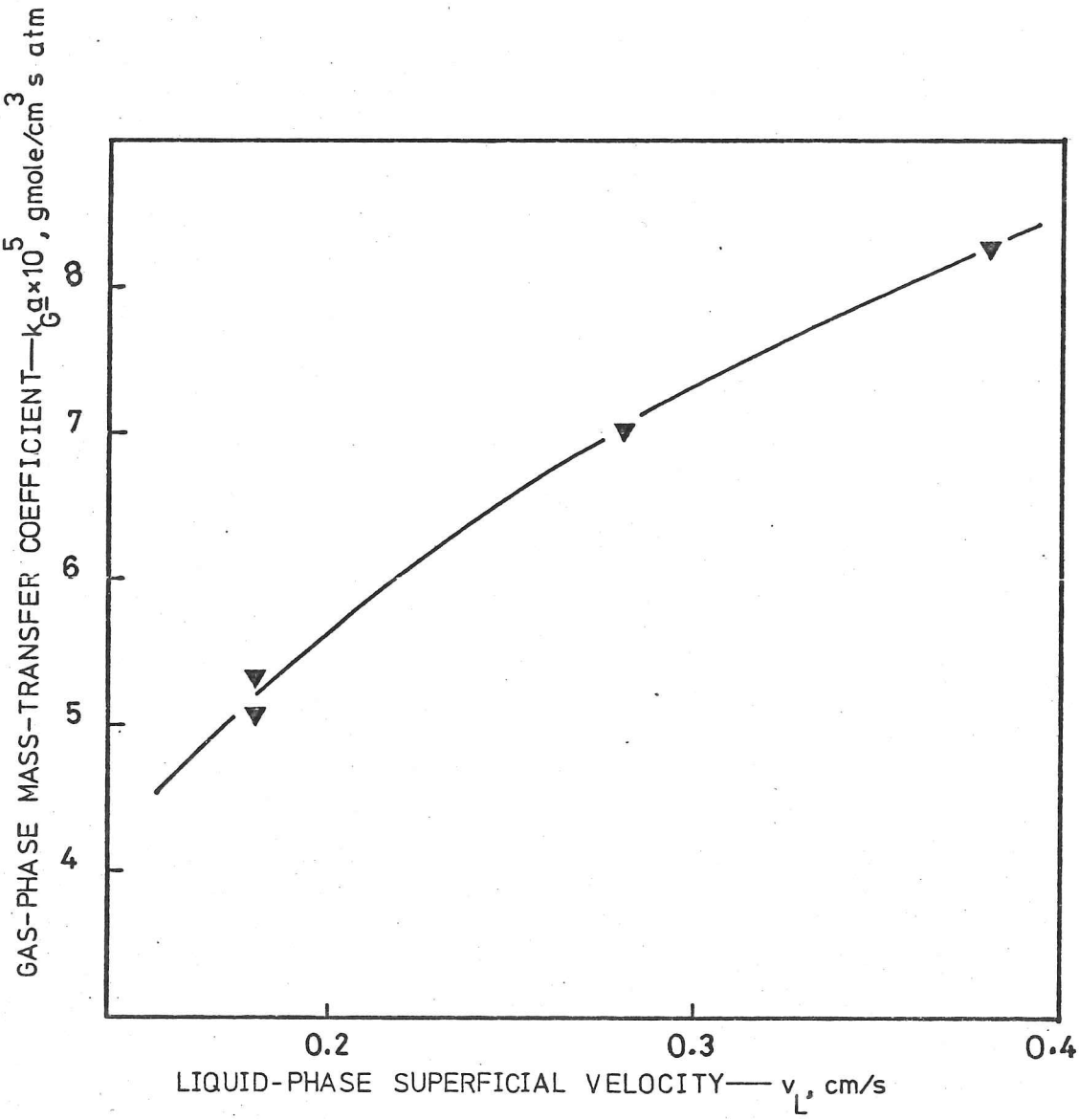

FIG. 3-11 DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTIONS INTO AIR—PACKED COLUMN; 0.64 cm RASCHIG RINGS; v_G = 20 cm/s; 25°C, 1 atm

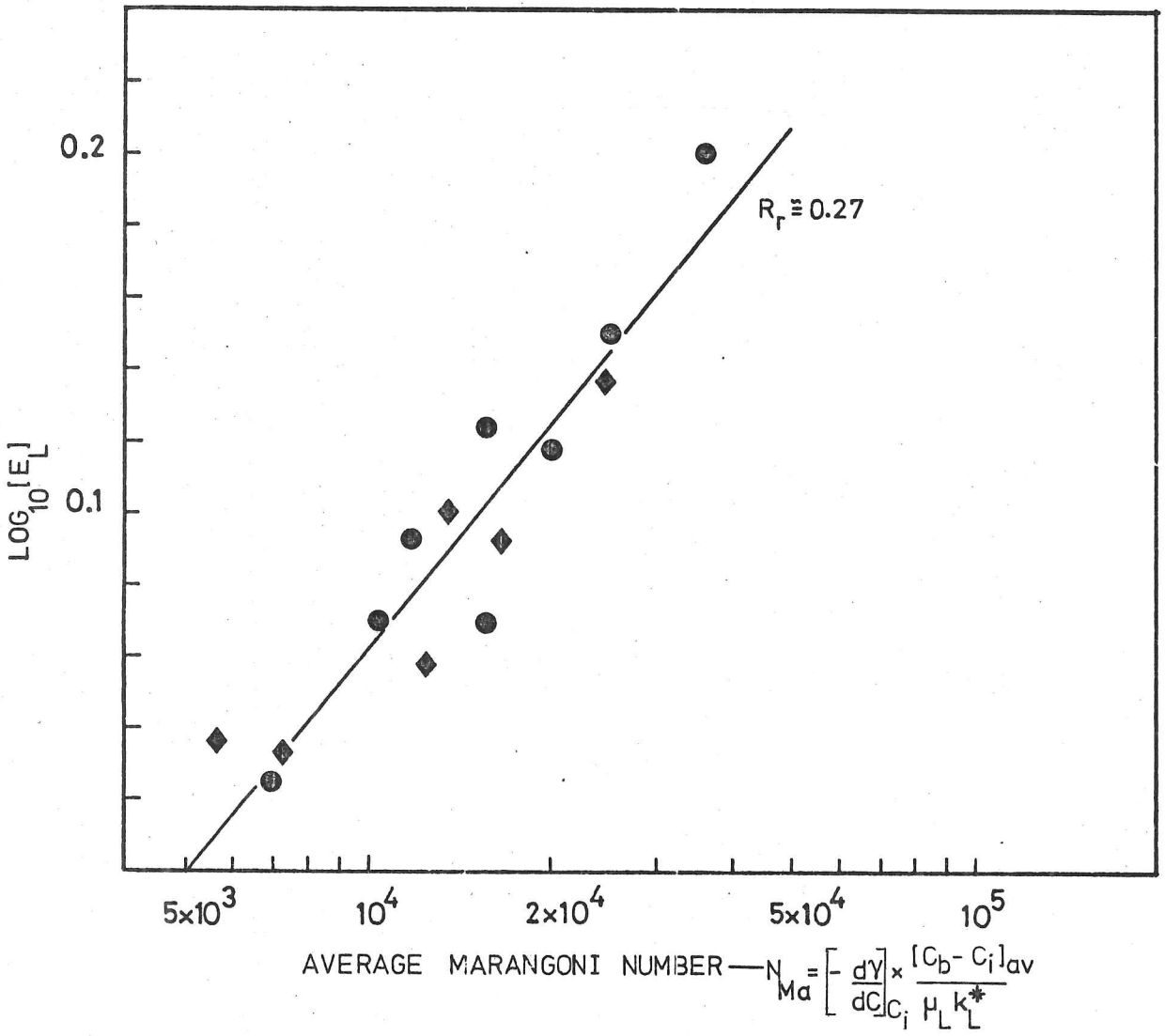

FIG. 3-12 EFFECT OF THE MARANGONI NUMBER ON THE LIQUID-PHASE ENHANCEMENT FACTOR — DESORPTION OF ACETONE IN THE PACKED COLUMN; 0.95 cm RASCHIG RINGS

3.4 Conclusions and Significance

The results show that Marangoni convection can substantially enhance the value of the liquid-phase mass-transfer coefficient in a packed column. It appears, however, that the convective instability has no measurable effect on the value of the gas-side mass-transfer coefficient under the conditions investigated. In effect, the "global" rate of transfer of solutes where the resistance to transfer lies almost entirely in the gas phase remains essentially unchanged by the occurrence of Marangoni convection. In the above experiments, for example, the occurrence of convective instability would have been unnoticed but for the simultaneous desorption of CO_2 to monitor the values of $k_L a$. An increase in the value of v_L was observed to result in a decrease in the value of E_L, while an increase in the value of v_G was found to increase the liquid-phase enhancement, although as suggested before there occurs, in general, a maximum.

A comparison of the values of E_L obtained in the packed column with those obtained by Brian *et al.* [B11] in a short wetted-wall column (and data presented in subsequent chapters of this thesis) appears to show that for systems susceptible to Marangoni instability it would in general be rash to extrapolate enhancement factors obtained under one set of hydrodynamic conditions to an entirely different set of hydrodynamic conditions, even for the transfer of the same solutes and for similar values of k_L^* and k_G.

CHAPTER FOUR

DESORPTION OF A) ACETONE AND B) ETHER FROM DILUTE AQUEOUS SOLUTIONS INTO AIR IN A MODIFIED STIRRED CELL

4.1 Introduction and Scope

Most of the previous work on the occurrence of Marangoni convection in gas-liquid systems has been carried out in relatively simple laboratory equipment. Data on the effect of Marangoni convection in gas-liquid systems where the bulk phases are in turbulent flow, or where the surface is periodically and randomly renewed or rejuvenated by eddies from the bulk reaching the interface, are scarce. In order to investigate the occurrence of the Marangoni effect in such systems it was decided to carry out some experiments in a stirred cell where the bulk gas and liquid phases are agitated by means of independent stirrers, and where the gas-liquid interfacial area is unambiguously known.

In addition, previous experimental work in stirred cells [A2] appeared to indicate that the liquid- and gas-phase mass-transfer coefficients could be varied independently over a wide range. It was therefore decided to test experimentally the validity of the speculations regarding the effect of k_G on the enhancement of the liquid-phase mass-transfer coefficient outlined in the previous chapter.

It should be emphasized that in industrial gas-liquid contactors the liquid and gas phases are generally in turbulent flow, and hence information regarding the effect of Marangoni convection in turbulent systems is of great practical importance. In turbulent systems, gradients of surface tension can in general arise either spontaneously due to the growth of random infinitesimal perturbations, as in initially stagnant liquid pools, or as a result of eddies from the bulk, of different

concentration from that existing at the surface, reaching or approaching the surface. The precise mechanism of surface renewal in such systems in the presence of Marangoni convection is not yet fully understood.

4.2 Experimental Apparatus and Procedure

The stirred cell employed in this work was a modified version of the type generally used in the past. The design features of the stirred cell normally used are available in the literature [D2]. In the usual case, the cell is operated either batchwise or in a continuous manner with respect to the liquid. In continuous operation, the inlet and outlet port-holes for the liquid are generally located at the bottom of the cell, and there occurs no overflow or removal of the surface layer. The result is that for either mode of operation, the surface tends to become contaminated due to the adsorption at the surface of unavoidable trace impurities present in the liquid. The effect of such contamination is likely to be severe at the relatively low stirring speeds employed in stirred cells. The adsorption of surface-active impurities results in the formation of an effectively rigid surface layer which inhibits, and in extreme cases totally suppresses, the occurrence of Marangoni convection. Preliminary experiments were carried out in a stirred cell of the usual design, and no evidence of the occurrence of Marangoni convection during the desorption of acetone and ether from dilute aqueous solutions into air was observed. Hence, it was decided to incorporate a suitable device into the design of the stirred cell which would effectively prevent the accumulation of impurities at the interface. This was achieved by means of a device which allowed for the overflow of the liquid at the surface, and is described in detail below.

The general features and layout of the apparatus used were similar to that used by Alper [A2,D4]. The stirred cell apparatus with the

"film-remover" in place is shown in Figure 4-1a. The film-remover, essentially an overflow device, consisted of a short piece of tubing, 7 cm in diameter and 4 cm high, fabricated out of nylon 66, and placed centrally with respect to the outer glass cell. The liquid and gas phases were agitated by means of two pairs of stirrers, a pair in each phase, the stirrers being fixed to two concentric contrarotating stirrer shafts. The outer shaft was kept aligned, as well as supported, by means of two bracket bearings, and had bushes on the inside at its two extremities to maintain the inner shaft in alignment and provide trouble-free rotation without excessive vibration. The inner shaft was further supported at the bottom of the cell by means of a nylon bearing.

The liquid-phase stirrers consisted of one 30 mm diameter twin-bladed turbine agitator to promote bulk mixing, and one 65 mm diameter four-bladed cruciform stirrer just skimming the interface. The gas-phase stirrers consisted of one three-bladed 30 mm diameter propeller to agitate the bulk gas, and a four-bladed 70 mm diameter inclined-turbine agitator, the blades being inclined at an angle of 60 degrees to the horizontal. The latter stirrer was located just above the liquid surface, the clearance being around 1.5 cm. The liquid-phase stirrers, as well as the stirrer shafts, were made of stainless steel, while the gas-phase stirrers were made of brass. Each of the stirrer shafts was connected by means of a system of pulleys to a reducing gear, which was itself coupled to a "Kopp" variator driven by means of a synchronous motor. The assembly enabled the stirrer speeds to be varied continuously over a wide range. The entire assembly of motors, variators, reducing gears, pulleys, bearings etc. was fixed onto a vertical rectangular block of chip-board. The layout of the experimental apparatus is shown in Figure 4-1b.

The details of the internal modifications to allow for liquid overflow are shown in Figure 4-1c. The liquid enters the cell through inlet

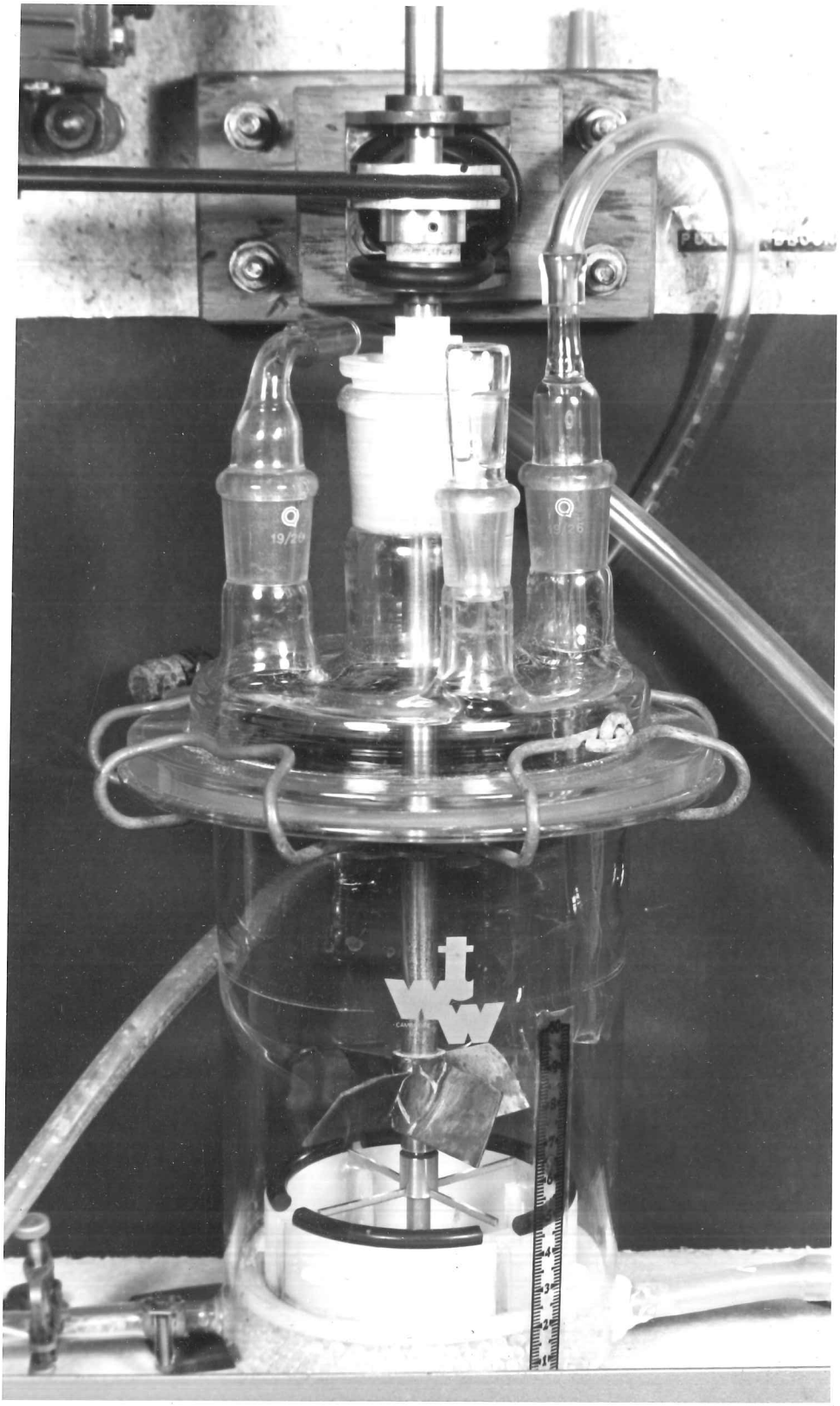

FIG. 4-1a THE STIRRED CELL APPARATUS

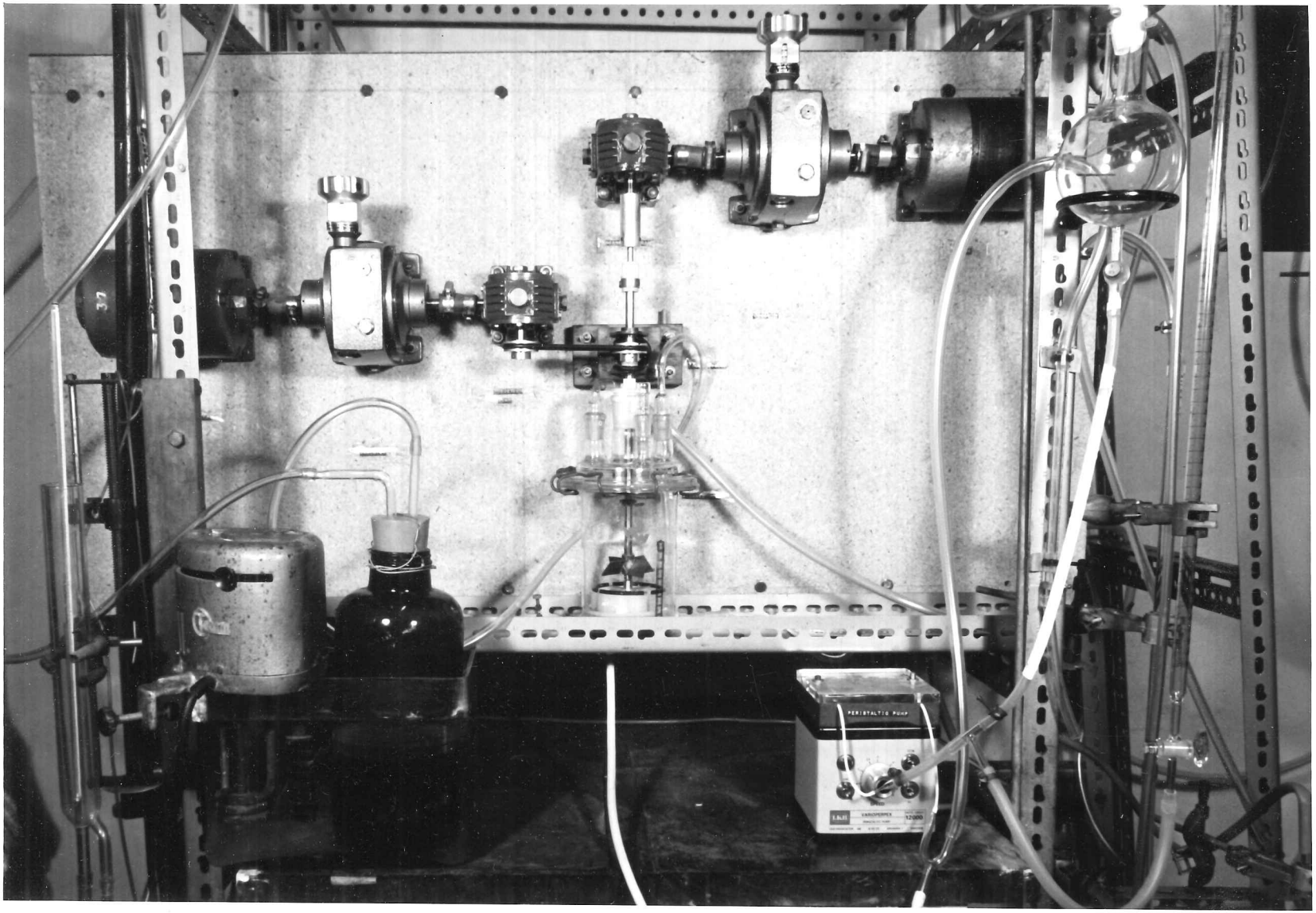

FIG.4-1b THE EXPERIMENTAL SET-UP FOR THE STIRRED CELL APPARATUS

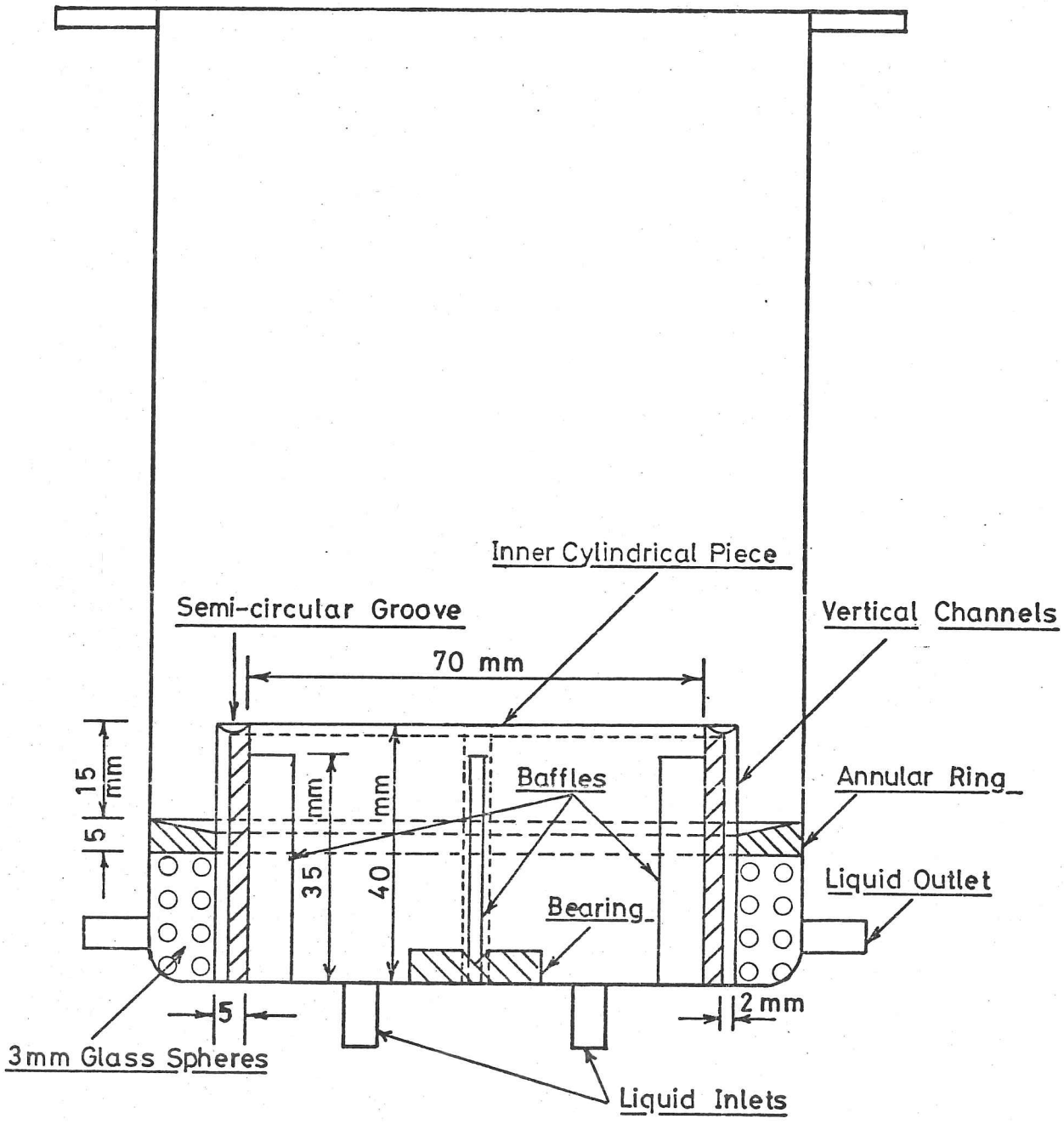

FIG. 4-1c INTERNAL DETAILS OF THE MODIFIED STIRRED CELL APPARATUS

port-holes located at the bottom of the cell and fills the interior of the cylindrical nylon piece. When the inner cylinder is full, the liquid overflows into a semi-circular peripheral groove, and then passes into four narrow vertical slots symmetrically machined into the outside of the cylindrical piece. From the slots the liquid flows into a pool of liquid maintained between the outer wall of the inner cylindrical piece and the inner wall of the glass cell. Mass transfer from this pool of liquid is prevented by means of a tightly fitting annular ring which is positioned just above the surface of the liquid. The upper surface of this ring was machined to have an inward taper to prevent liquid from being retained on the ring. The ring was positioned such that the height of the slots exposed was around 1.6 cm. The liquid from this external pool was removed via two exit tubes, and the height of the liquid pool was maintained just below the inner upper face of the annular ring by means of a simple external constant-level device. To minimise the residence time of the fluid in this outer annular pool of liquid, it was filled with 3.2 mm diameter glass beads. The inner cylindrical piece was attached to the base of the glass vessel by using epoxy resin as the binding agent. The glass surface was roughened prior to making the joint with carborundum powder.

It had been hoped initially to minimise the wall thickness of the inner cylindrical piece so that the area of liquid exposed to the gas in the groove would be negligible. However, to prevent distortion during fabrication a wall thickness of approximately 5 mm was found necessary. To prevent an excessive transfer area from being exposed to the gas as a result of the groove, suitable sections of O-rings were placed in the groove leaving open only those parts of the groove immediately adjacent to the slots. In calculating the mass-transfer coefficients it was

assumed that the interfacial area of contact was equal to the cross-sectional area of the inner nylon piece less the area occupied by the cruciform stirrer; this area was equal to 36.6 cm^2. The cylindrical piece was provided with four symmetrically located baffles to avoid vortex formation. The cover of the glass cell had several standard cone-and-socket quickfit joints, a pair of which were selected as the gas inlet and exit port-holes. The stirrer shafts passed into the vessel through a mercury seal.

The entire apparatus was assembled in a constant-temperature room maintained at approximately 25°C. The auxiliary apparatus was similar to that described for the packed column. Carbon dioxide was desorbed from the liquid phase to monitor the values of k_L in the absence as well as in the presence of Marangoni convection. Acetone and ether were desorbed from dilute aqueous solutions into air to generate the Marangoni convection. The rate of desorption of acetone from dilute aqueous solutions was used to calculate the values of k_G after correcting for the small liquid-phase resistance.

The gas flow rate for most of the experiments was 210 cm^3/s. The liquid flow rate was maintained constant at 1 cm^3/s for all the experiments. The gas-phase mass-transfer coefficient in apparatus of this type is known to be independent of gas flow rate over the range normally encountered in practice [H3]. The gas phase was assumed to be completely mixed over the range of stirring speeds investigated. Because of the uncertainty introduced as a result of the overflow of the liquid, the arithmetic average of the inlet and the outlet liquid concentration was used to calculate the average driving force. The maximum change in the concentration of dissolved carbon dioxide in the liquid was around 50%. The analytical and sampling techniques were the same as those discussed

with respect to the packed column. In the case of experiments involving the desorption of ether, accurately prepared concentrated aqueous solutions were stored in the glass reservoir connected to the micropump. Flexible silicone tubing was used for all parts of the system, upto the inlet port-holes of the stirred cell, in contact with the aqueous solutions of acetone and ether. Materials of construction were chosen on the basis of their demonstrated resistance to the solutions used over relatively long periods of exposure. Precautions similar to those discussed with respect to the packed column were taken to avoid any accidental contamination.

The time required for steady-state to be reached was determined from preliminary experiments. Because of the relatively low liquid flow rate used, a fairly long period of time (about 35 minutes) was allowed to pass before samples were taken.

To execute a run the liquid and the air flow rates were adjusted to the desired values, and the flow rate of the micropump was adjusted to give the desired concentration of the solute. The gas- and liquid-phase stirrers were started, and their speeds adjusted to the required values. After allowing sufficient time for steady-state to be reached, samples of inlet and outlet liquid were obtained. Because of the relatively large gas flow rate, the concentration of CO_2 in the outlet air was small enough to be neglected. For the determination of the gas-phase mass-transfer coefficient, the concentration of acetone in the outlet air stream was measured.

In the present investigation the liquid-phase stirrer speed was varied from 24 to 70 RPM (revolutions per minute), and the gas-phase stirrer speed was varied from 100 to 500 RPM.

4.3 Results and Discussion

The maximum liquid- and gas-phase stirrer speeds employed were in effect determined by the appearance of the liquid surface. Gas stirrer speeds in excess of 500 RPM resulted in unacceptably large distortion of the liquid surface, and the surface could no longer be considered to be flat. Similarly, liquid-phase stirrer speeds in excess of 70 RPM also caused considerable distortion of the interface. Previous workers [A2,D4] have reported using maximum speeds roughly twice as high as those used in this work. In those previous investigations, however, no attempt was made to obtain a clean interface, and it appears likely that the resulting contaminated interfaces were less susceptible to surface rupture, possibly due to an appreciable surface elasticity resulting from the accumulation of contaminants at the interface.

In the course of preliminary experiments with the modified cell, it was observed that the liquid-phase enhancement showed a gradual increase with time for a fixed set of experimental conditions. After approximately a month of operation, however, the system stabilised and reproducible results were obtained. It appears that initially some unknown contaminant was present in the system which was gradually being removed in the course of normal operation. A possible source of this contamination could be the epoxy resin used to bind the film-remover to the bottom of the glass cell. The resin probably contained a substance which was leached out by the aqueous solutions employed, without apparently significantly affecting the binding properties.

Figure 4-2 shows the effect of the liquid-phase stirrer speed on the value of k_L^*. An increase in the liquid stirrer speed from 24 to 65 RPM resulted in an increase in the value of k_L^* from 0.0029 cm/s to 0.008 cm/s. The effect of a variation in the gas-phase stirrer speed on

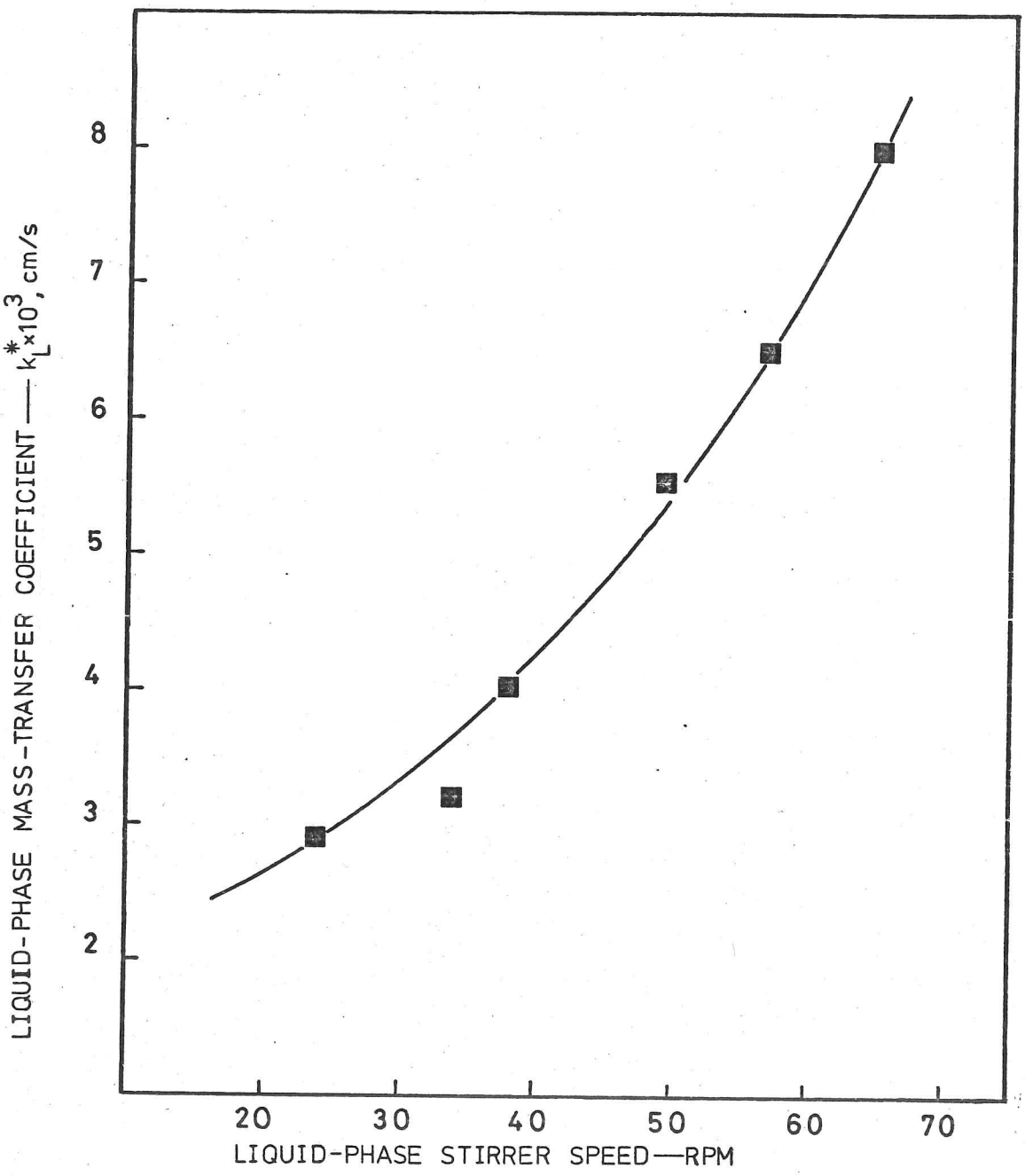

FIG. 4-2 DESORPTION OF CO_2 FROM WATER INTO AIR IN THE STIRRED CELL ; N_G = 100 RPM ; 25° C, 1 atm

the value of k_L^* is shown in Figure 4-3. It is seen that in the range investigated the intensity of agitation in the gas phase had no measurable effect on the value of the liquid-phase mass-transfer coefficient.

A) Desorption of Acetone

The effect of acetone desorption on the values of k_L is shown in Figure 4-4. It is seen that desorption of acetone results in a several-fold increase in the value of the liquid-phase mass-transfer coefficient due to the Marangoni convection induced by the desorption of acetone. The figure shows that in the range investigated (0 - 2.14 wt. %), an increase in the concentration of acetone in the inlet liquid substantially increases the value of k_L, this being a characteristic feature of Marangoni convection in general. For a liquid-phase stirrer speed of 24 RPM and a gas-phase stirrer speed of 100 RPM, k_L is seen to be enhanced by a factor of more than 4 for an inlet concentration of acetone in the liquid of about 2.1 wt. %. The change in the concentration of acetone in the liquid was negligible.

As discussed earlier, the occurrence of surface-tension driven flow in turbulent systems is a fairly complex phenomenon. Consider for the sake of analysis an agitated gas-liquid system having an essentially plane interface. Let us assume that a volatile solute which depresses the surface tension is being desorbed from the liquid into the gas phase. As a result of the agitation, eddies of liquid approach the surface from the bulk and spread outwards on reaching the surface, resulting in surface renewal. In the case considered, the average solute concentration at the interface, relative to that in the bulk, is dependent on the ratio of the resistance to transfer in each of the phases, and is less than unity. Hence, the eddies of liquid on reaching the surface result in the occurrence of localised areas of low surface tension, giving rise to

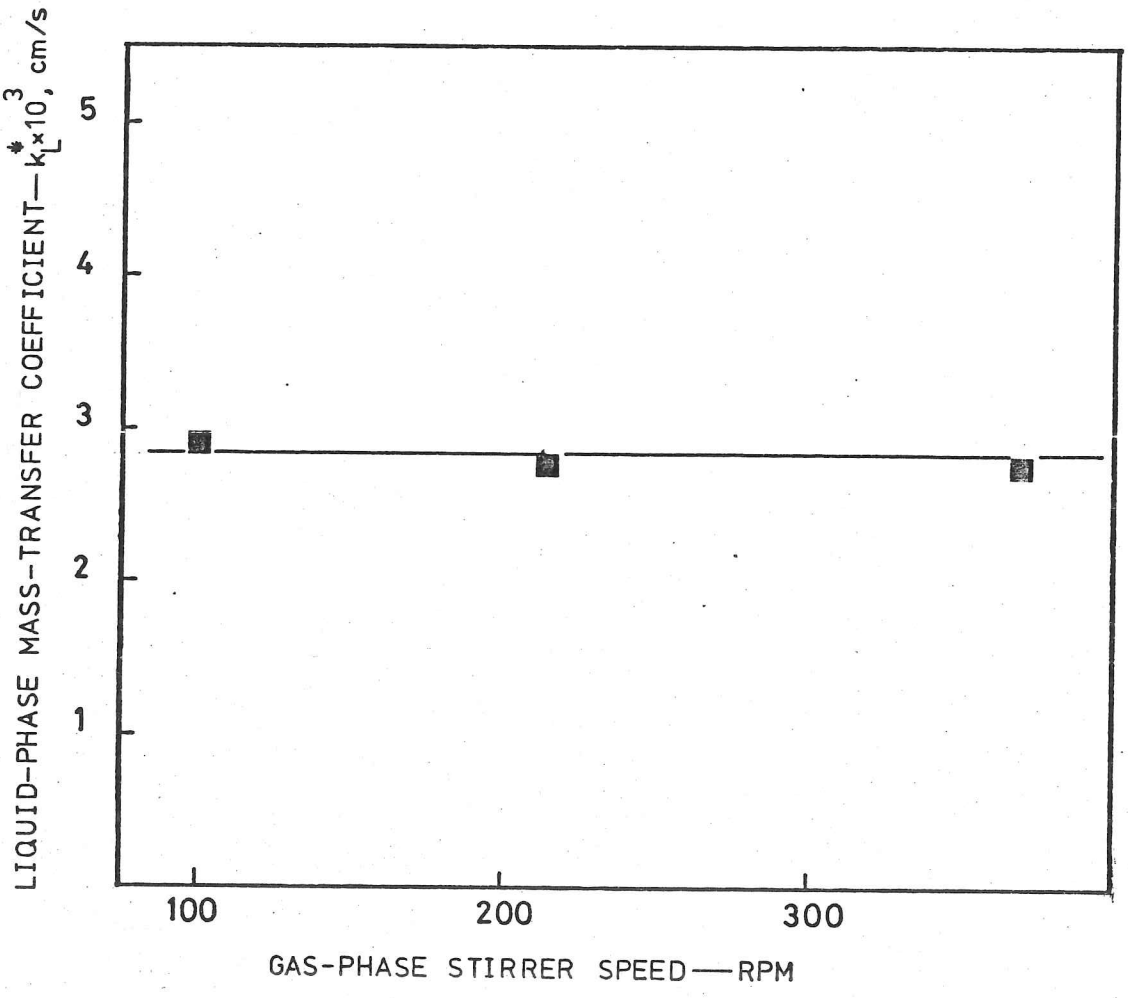

FIG. 4-3 DESORPTION OF CO_2 FROM WATER INTO AIR IN THE STIRRED CELL; $N_L = 24$ RPM; 25° C, 1 atm

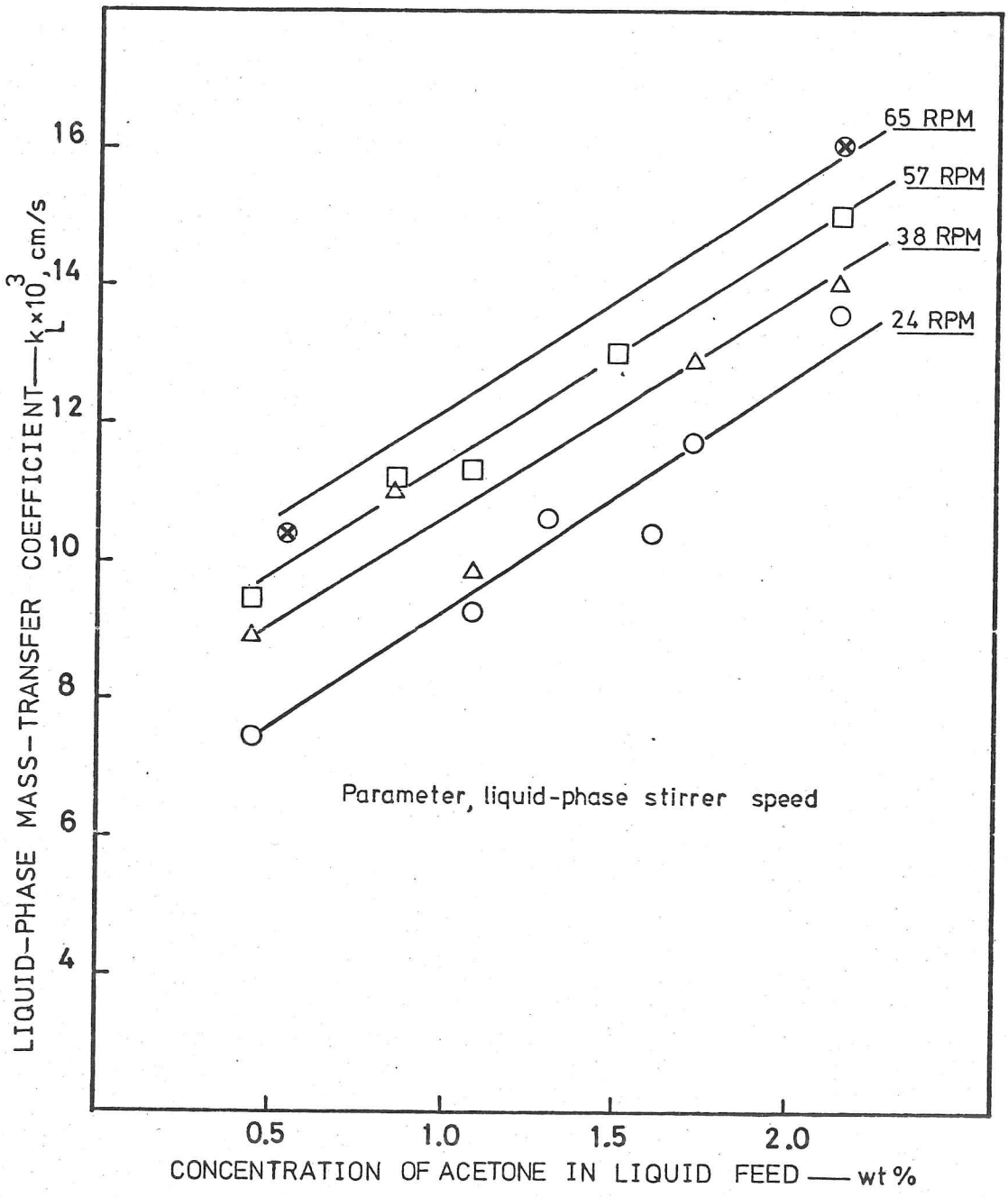

FIG. 4-4 DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE—STIRRED CELL; N_G=100 RPM; 25° C, 1 atm; G=210 cm^3/s, L=1 cm^3/s

macroscopic surface-tension gradients which tend to reinforce the spreading motion. However, if the solute is strongly adsorbed at the interface, the spreading motion will be inhibited because it will result in an unfavourable redistribution of the solute in the surface [B3], generating surface forces which tend to oppose the spreading motion. The net effect on the motion is thus dependent on the resultant of the two opposing forces.

It should be noted that surface tension is a dynamic phenomenon where surfaces are being created, expanded or contracted. In the absence of mass-transfer effects, the surface tension of a freshly-exposed surface of a dilute aqueous solution will in general be close to that of water and, in the case where the solute depresses the equilibrium value of the surface tension, the instantaneous value of the surface tension will then fall with increasing time as the solute diffuses towards the surface, until the concentration distribution which accords with Gibbs' law is reached. In some cases the time required for the equilibrium or static value to be reached is essentially negligible compared to the time-scale involved, and the static surface tension can be assumed to be reached "instantaneously", e.g. in the du Noüy tensiometer for measuring surface tension. In some cases, however, the time required may be of the order of several seconds. Bakker et al. [B1] and Mayr [M2] have classified solutes on the basis of the time required for a freshly exposed surface to virtually reach its equilibrium surface tension in the absence of interfacial mass transfer. In general, very strongly adsorbed solutes require an appreciable time before reaching the equilibrium value, and generally impede surface motion. Employing the model of Bakker et al., Mayr has shown that, in the concentration range of interest to the present work, the time required in the case of aqueous solutions of acetone is of the order of micro-seconds, and in the case of

aqueous solutions of ether the time required is of the order of a fraction of a milli-second. Although the above analysis ignored mass transfer across the gas-liquid interface, Mayr has shown that the characteristic-time for mass transfer across the interface is several orders of magnitude larger than the characteristic-time for surface-tension equilibration for the solutes and conditions of interest to this work, and hence the results of the analysis are also applicable to the case where mass transfer occurs across the interface in the context of this dissertation.

In addition, in cases where the spreading motion at the gas-liquid interface, due to the fluid eddies reaching the interface, is reinforced by the surface-tension forces generated, the possibility exists of the occurrence of Marangoni instability due to the growth of random infinitesimal perturbations in the unstable direction of transfer. Such instability will occur in regions of the surface where the concentration gradients normal to the surface are large enough for the critical Marangoni number of the system to be exceeded. Any finite motion as a consequence of Marangoni instability will cause additional surface renewal. The interactions that occur in turbulent systems are therefore rather complex, and it is not possible to quantify them at present. The morphology of the convective motion at the surface would in general be influenced by the bulk turbulence, particularly in highly agitated systems.

It is interesting to note that in the case of turbulent systems localised macroscopic Marangoni convection may occur, albeit momentarily, even when the direction of solute transfer is such that the system is stable with respect to infinitesimal disturbances (i.e. Marangoni instability). This is due to the effect of eddies reaching the surface from the bulk and creating areas of sufficiently low surface tension. If, however, the dominant surface forces are those generated by the compression of the solute in the adsorbed layer, surface renewal will be

inhibited and the value of the mass-transfer coefficient may be actually less than the value in the absence of the Marangoni effect. The inhibition of surface renewal would be further enhanced if the time required for surface-tension equilibration is appreciable relative to the average exposure-time. Dynamic effects are then important and equilibrium considerations alone are not sufficient.

The effect of the liquid-phase stirrer speed on the enhancement of k_L is shown in Figure 4-5 for acetone concentrations in the liquid of 1.0 and 2.0 wt. %. The figure shows that, other things remaining equal, an increase in the intensity of agitation results in a decrease in the liquid-phase enhancement factor E_L. This is probably because an increase in the degree of agitation increases not only the value of k_L^* but, in addition, the consequent decrease in the average exposure-time results in a decrease in the magnitude of the effective surface-tension gradients, and hence in relatively less reinforcement of the existing surface flow.

The equilibrium surface tension of a 2 wt. % aqueous solution of acetone is roughly 15% less than that of pure water, and this lowering of the magnitude of the surface tension might by itself result in a change in the value of k_L^*. However, previous work [cited in D6] appears to indicate that for stirred cells similar to the one used in this work, the value of k_L is virtually independent of the magnitude of the surface tension of the liquid in the cell for the range of interest to the present work.

The effect of the gas-phase stirrer speed on the value of k_L during the desorption of acetone is shown in Figure 4-6 for liquid-phase stirrer speeds of 24 and 38 RPM. The acetone concentration in the liquid was 1.08 wt. %, and the gas-phase stirrer speed was varied from about 100

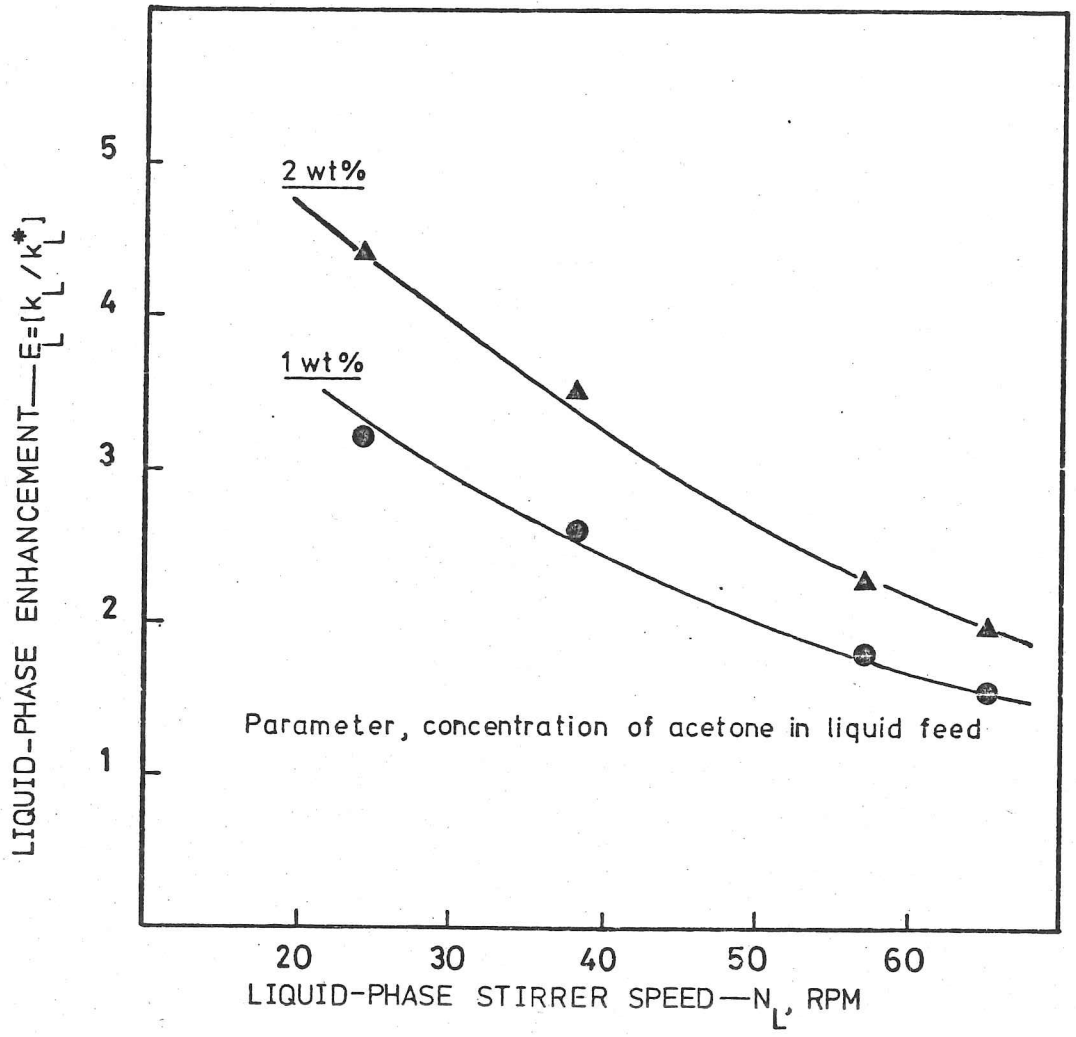

FIG.4-5 EFFECT OF THE LIQUID-PHASE STIRRER SPEED ON THE LIQUID-PHASE ENHANCEMENT FACTOR —— STIRRED CELL; N_G = 100 RPM; G=210 cm^3/s, L=1 cm^3/s

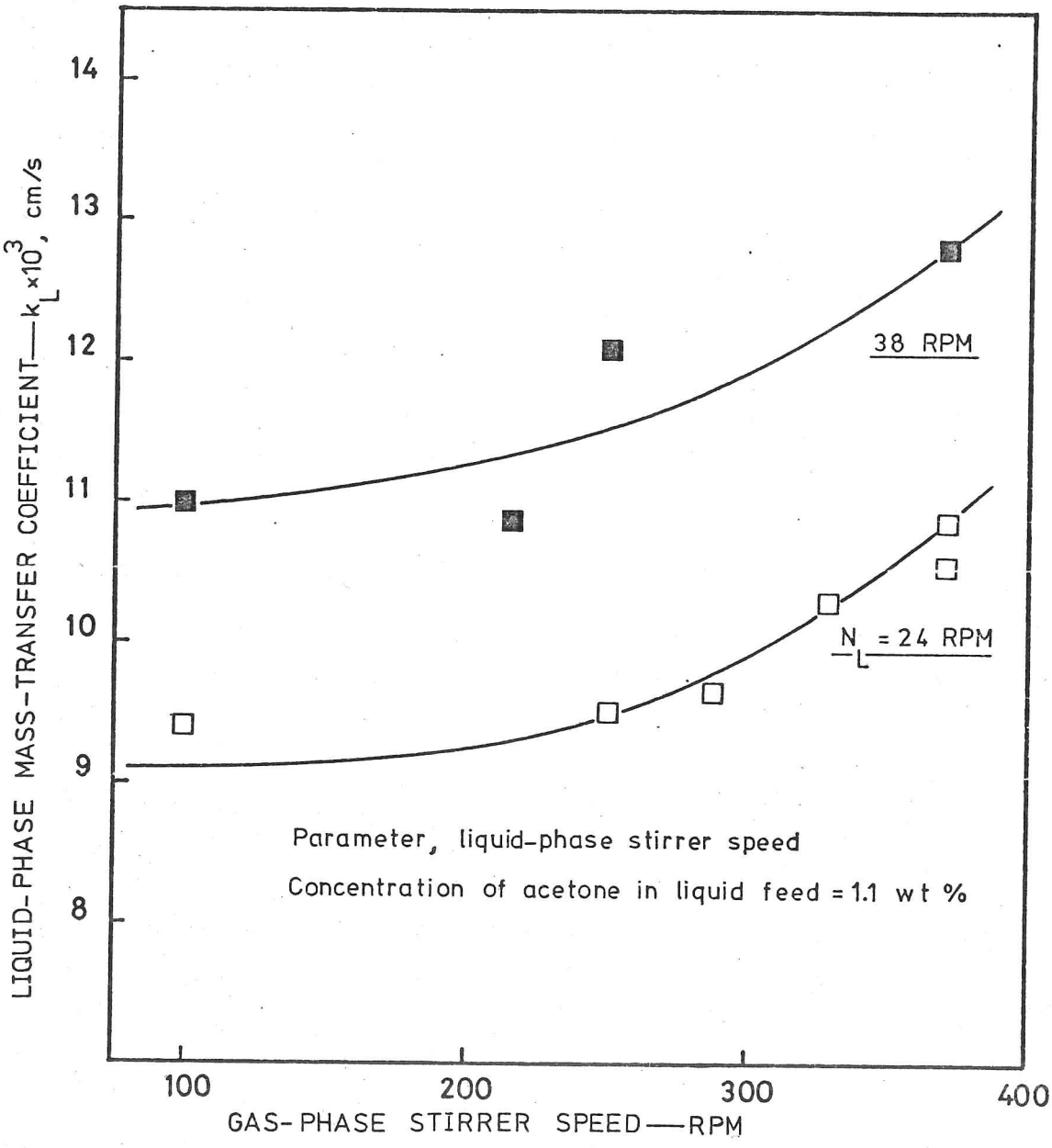

FIG. 4-6 DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ACETONE — STIRRED CELL; G=210 cm^3/s, L= 1 cm^3/s; 25°C, 1 atm

to 400 RPM. Based on data reported by Alper [A2,D4] a three-fold variation in the value of k_G was anticipated, and hence, based on the speculations outlined in the previous chapter, a substantial effect of the variation of the gas-phase stirrer speed on the value of k_L was expected. The observed effect which is shown in Figure 4-6 was, however, very small. An increase of only about 20% in the value of k_L was observed over the range of gas-phase stirrer speeds investigated.

Experiments were therefore carried out to determine the values of k_G as a function of the stirring speed in the gas phase. It was found that for the apparatus used in this work, the increase in the value of k_G due to an increase in the gas stirrer speed was much less than that anticipated on the basis of Alper's work. It was found that an increase in the gas stirrer speed from 100 to 400 RPM resulted in an increase in the value of k_G of approximately 50%. The results obtained are shown in Figure 4-7. The data plotted further show that it is likely that for stirred cells, too, the Marangoni effect has no measurable effect on the gas-side mass-transfer coefficient. Levenspiel and Godfrey [L1] have also measured the effect of the gas-phase stirrer speed on k_G in a similar type of apparatus. The relative increase in k_G obtained by changing the gas stirrer speed from 100 to 400 RPM in their work is in fairly good agreement with the relative increase obtained in this work over the same range of stirrer speeds. An increase in the value of k_G for a fixed gas flow rate results in a decrease in the average driving force for acetone desorption because of an increase in the concentration of acetone in the gas phase. Under the conditions of this investigation, however, the maximum relative decrease in the driving force, due to an increase in the stirrer speed in the gas phase, was computed to be around 5%. Because of the relatively large gas flow rates, the acetone concentration in the outlet gas was approximately 10 to 15 per cent of

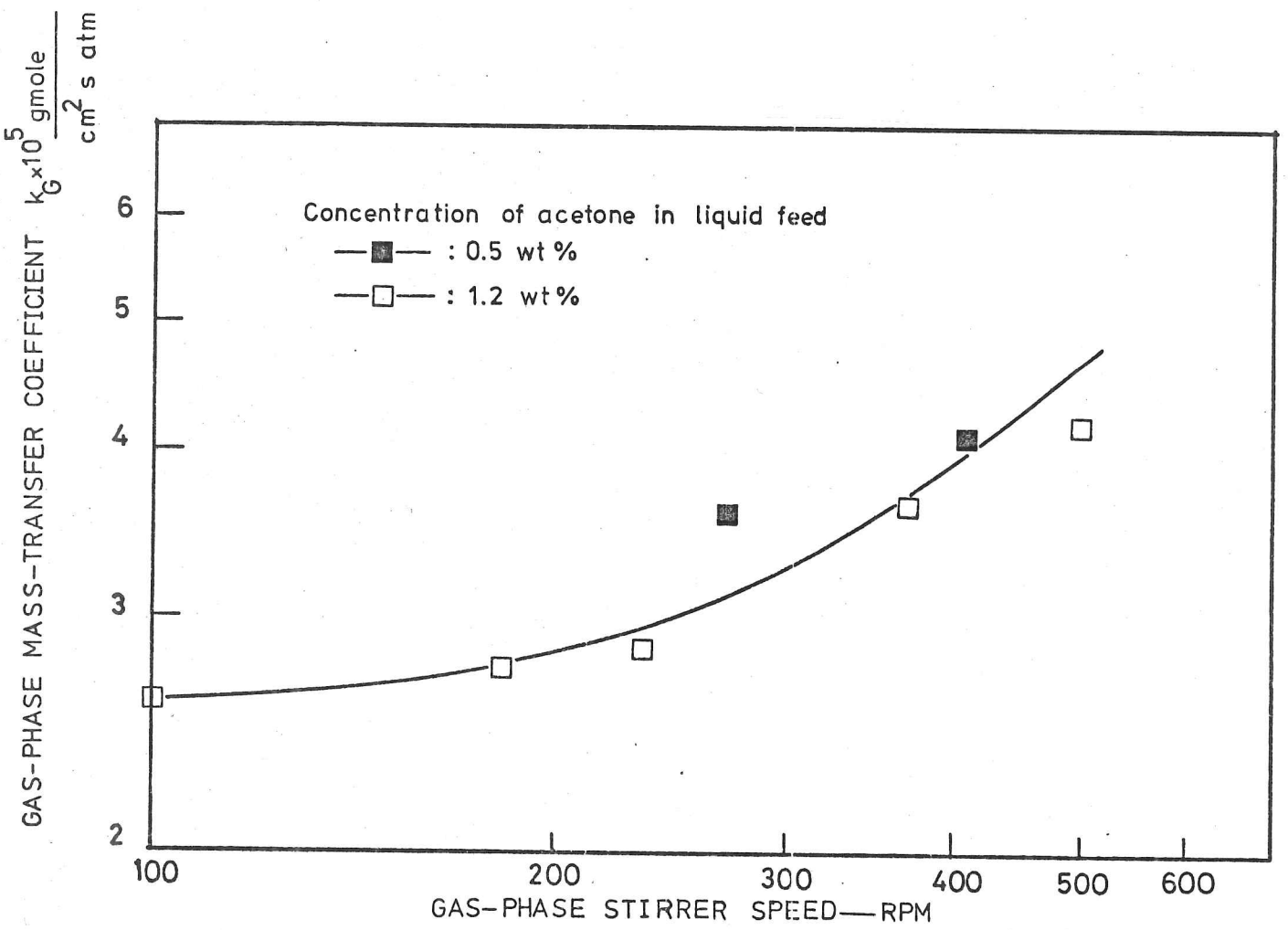

FIG.4-7 DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTIONS INTO AIR IN THE STIRRED CELL ; G=100 cm^3/s, L=1 cm^3/s ; N_L=38 RPM ; 25° C, 1 atm

its saturation value in the range studied.

B) Desorption of Ether

Some experiments were carried out to investigate the effect of Marangoni convection induced by the desorption of ethyl ether from extremely dilute aqueous solutions. It should be noted that for the desorption of ether, the mass-transfer resistance in both the phases is significant. Figure 4-8 shows the effect of the liquid-phase stirrer speed on the enhancement of the liquid-side mass-transfer coefficient, E_L, during desorption of ether. The concentration of ether in the inlet liquid was 0.12 wt. %, and the gas-phase stirrer speed was held constant at 183 RPM. It can be seen that for a given enhancement in the value of k_L, the concentration of ether required in the inlet liquid is very much smaller than the corresponding acetone concentration under otherwise identical conditions; the diminution of the magnitude of the surface tension was, however, roughly the same, with that for the aqueous solutions of ether being somewhat less than for the aqueous solutions of acetone.

The effect of the gas-phase stirrer speed on the value of the liquid-phase mass-transfer coefficient during ether desorption is shown in Figures 4-9 and 4-10 for concentrations of ether in the inlet liquid of 0.12 and 0.18 wt. %, respectively. The figures show that for ether desorption, the liquid-phase mass-transfer coefficient is essentially independent of k_G over the range investigated. This is in contrast to the case of desorption of acetone where the value of E_L was shown to increase because of an increase in the value of k_G. There is a significant change (roughly 20%) in the concentration of ether in the liquid phase as the liquid flows through the cell. However, calculations showed that the change in the value of the average overall driving force for ether desorption, due to the variation in the value of k_G, was

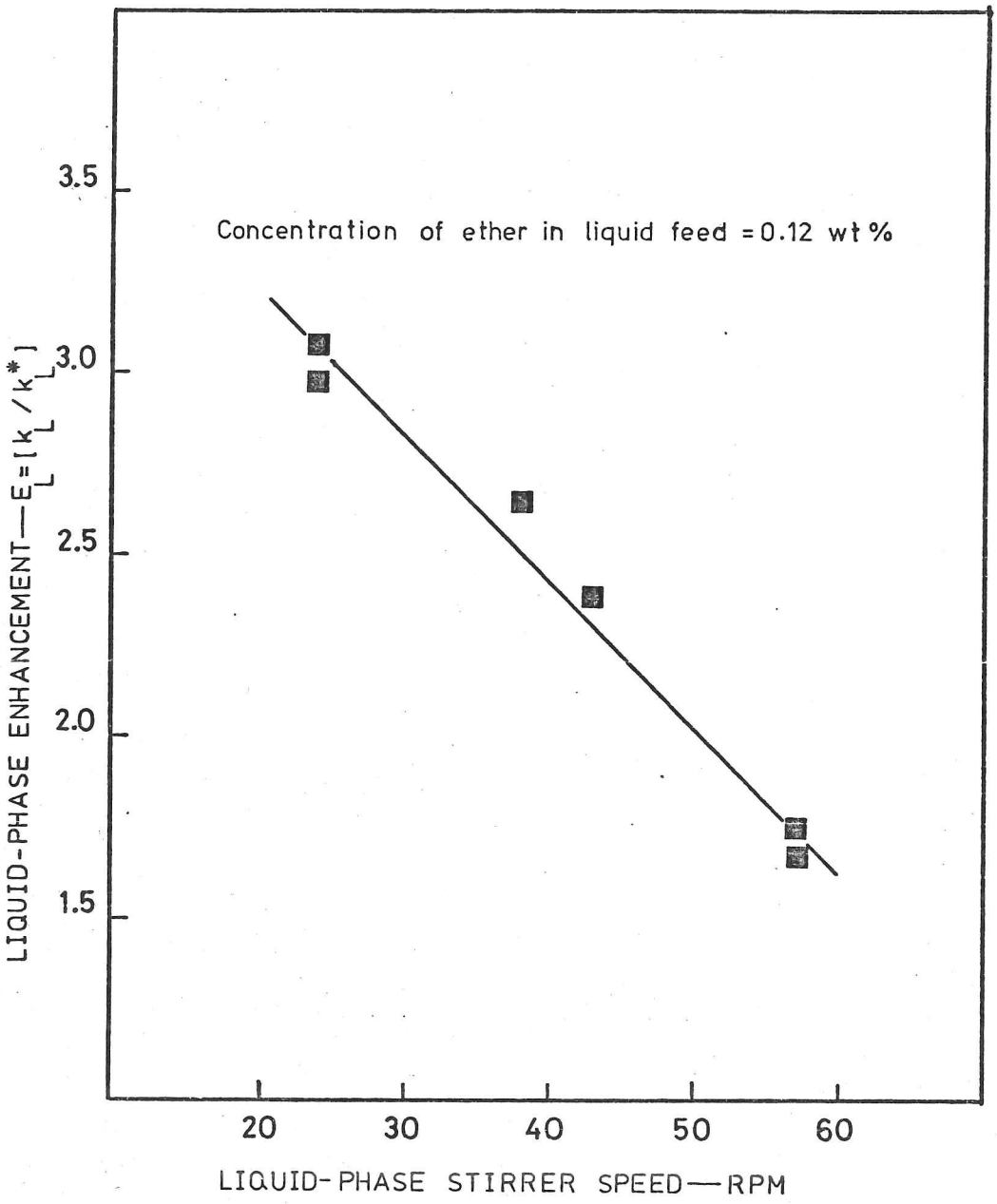

FIG. 4-8 EFFECT OF THE LIQUID-PHASE STIRRER SPEED ON THE ENHANCEMENT OF THE LIQUID-PHASE COEFFICIENT — STIRRED CELL; N_G = 183 RPM; L = 1 cm^3/s, G = 210 cm^3/s; 25° C, 1 atm

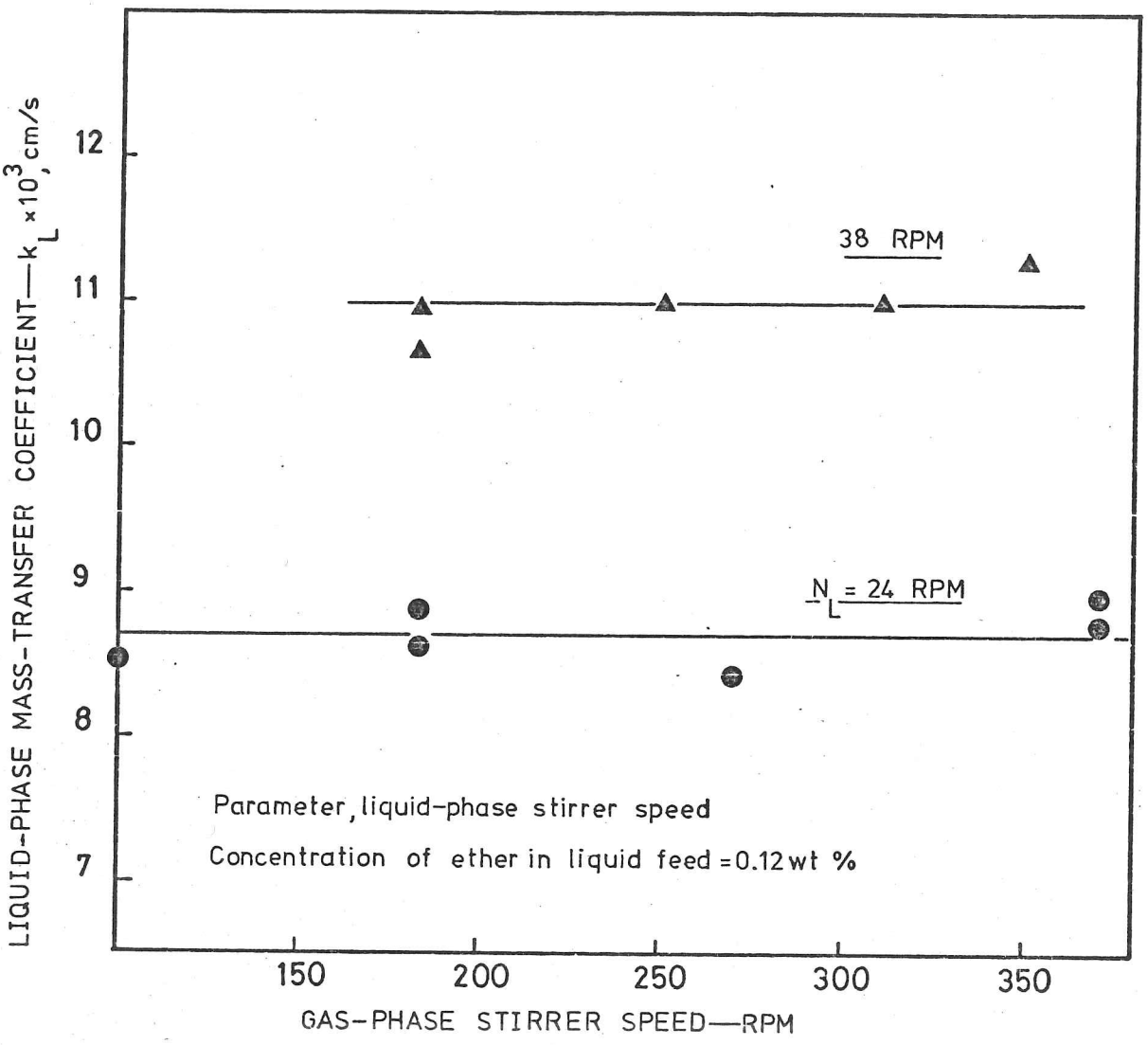

FIG. 4-9 DESORPTION OF CO_2 FROM WATER INTO AIR DURING SIMULTANEOUS DESORPTION OF ETHER—STIRRED CELL; G=210 cm^3/s, L=1 cm^3/s; 25° C, 1atm

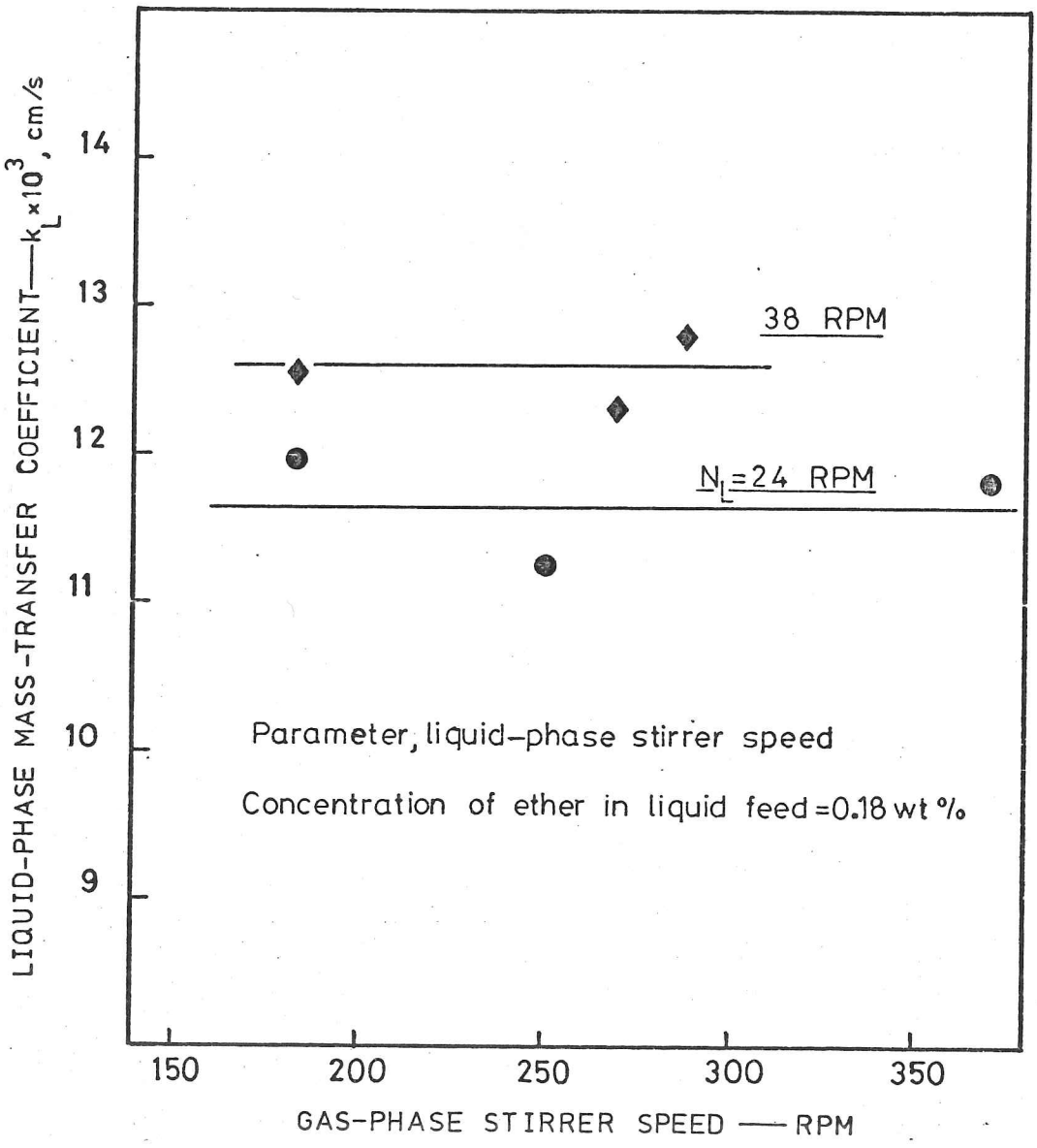

FIG. 4-10 DESORPTION OF CO_2 FROM WATER INTO AIR DURING THE SIMULTANEOUS DESORPTION OF ETHER—STIRRED CELL; G = 210 cm^3/s, L = 1 cm^3/s; 25° C, 1 atm

negligible for the range investigated.

As stated in the introduction to this chapter, it was hoped that the speculations regarding the effect of k_G on E_L could be tested in the stirred cell employing acetone and ether as the Marangoni-effect generating solutes. The results obtained appear to lend some support to the speculations; however, due to the relatively small change in the value of k_G over the range investigated, no firm conclusions can be drawn. A matter of some uncertainty, in addition, is the effect of a change in the compressibility of the adsorbed layer at the surface, due to a change in the concentration of the solute at the interface, on the intensity of the surface-tension driven convective motion at the interface.

Aqueous solutions of ether as well as acetone are less dense than pure water. Hence, the possibility existed that during desorption of the solutes sufficiently large destabilising density gradients developed for Rayleigh instability to manifest itself. Therefore, the Rayleigh number for the system, based on the concentration gradients established over the average exposure-time, was calculated as suggested by Clark and King [C1] and Blair and Quinn [B6], and compared with the value of the critical Rayleigh number (determined on the basis of an initially quiescent liquid). The calculations showed that the Rayleigh number was well below the critical value for the entire range investigated, and hence it was assumed that density effects were not significant.

4.4 Conclusions and Significance

The desorption of acetone and ether from dilute aqueous solutions into air in a stirred cell was found to result in considerable enhancement of the liquid-phase mass-transfer coefficient over the range

investigated. An increase in the intensity of agitation in the liquid phase was found to decrease the liquid-phase enhancement, other things remaining equal. During the desorption of acetone, the liquid-phase enhancement was found to increase with an increase in the value of k_G; for ether desorption, however, the liquid-phase enhancement appeared to be virtually independent of k_G over the range investigated. Since the range of variation of k_G was small, further work is needed before any definite conclusions can be drawn regarding the validity or otherwise of the speculations regarding the effect of k_G on the liquid-phase enhancement in general.

CHAPTER FIVE

DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTIONS INTO AIR IN A WETTED-WALL COLUMN

5.1 Introduction and Scope

A critical factor in assessing the importance of Marangoni instability for a given system is the rate of growth of the intensity of the convective motion subsequent to initiation. It is not sufficient for a complete quantitative analysis to predict only the value of the critical Marangoni number and, therefore, obtain information about the potential stability of the system. For a system susceptible to convective instability, it is also essential to know if, under the conditions of operation, the ensuing convective motion will have time to grow to a magnitude sufficiently large to have a measurable effect on the rate of gas absorption. Such information cannot be obtained from a linear stability analysis of the system. A non-linear analysis, possibly involving the numerical solution of the appropriate transport equations, could probably yield the desired information provided a sufficiently detailed and physically realistic model could be constructed. A certain amount of arbitrariness, however, would be involved in the choice of the morphology and magnitude of the initial disturbances, and at present it seems unlikely that meaningful results could be obtained in general. Nakaike et al. [N1] have solved numerically the relevant convective-diffusion equations for a 2-dimensional liquid-liquid system for an arbitrary initial disturbance.

In order to obtain some information regarding the rate of growth of Marangoni instability, it was decided to carry out some experiments in a short wetted-wall column. Brian et al. [B11] reported that in

short wetted-wall columns the Marangoni instability, induced by desorption of solutes which lower the surface tension, increased the values of k_L several-fold. No attempt was made by them, however, to investigate the rate of growth of the convective instability. An important observation made by Brian et al. was that the Marangoni effect had apparently no effect on the value of k_G.

5.2 Apparatus and Procedure

The wetted-wall column (diameter = 2.38 cm) was the same as that used by Alper [A2], and is shown in Figure 5-1. By sliding the liquid receiver and PTFE collar up or down, the height of the liquid film exposed to the gas could be varied. The collar was provided with three vertical channels to prevent the build-up of a contaminant film on the exposed surface of the flowing liquid. The general design features of wetted-wall columns have been adequately discussed elsewhere in the literature [D2]. To prevent the formation of ripples on the surface of the film, relatively short heights (less than 7 cm) were used. Surface-active agents could not be used to suppress ripple formation because of their inhibitory effect on Marangoni convection. The apparatus was operated in a co-current manner with both gas and liquid flowing downwards.

Acetone was desorbed from dilute aqueous solutions into air to initiate convective instability. In most of the experiments the concentration of acetone in the inlet liquid was 0.5 wt. %. A few experiments, however, were carried out at a concentration of 0.25 wt. %. The change in the concentration of acetone in the liquid phase as a result of desorption was negligible. The rate of desorption of acetone was measured to calculate the values of k_G. Carbon dioxide was simultaneously

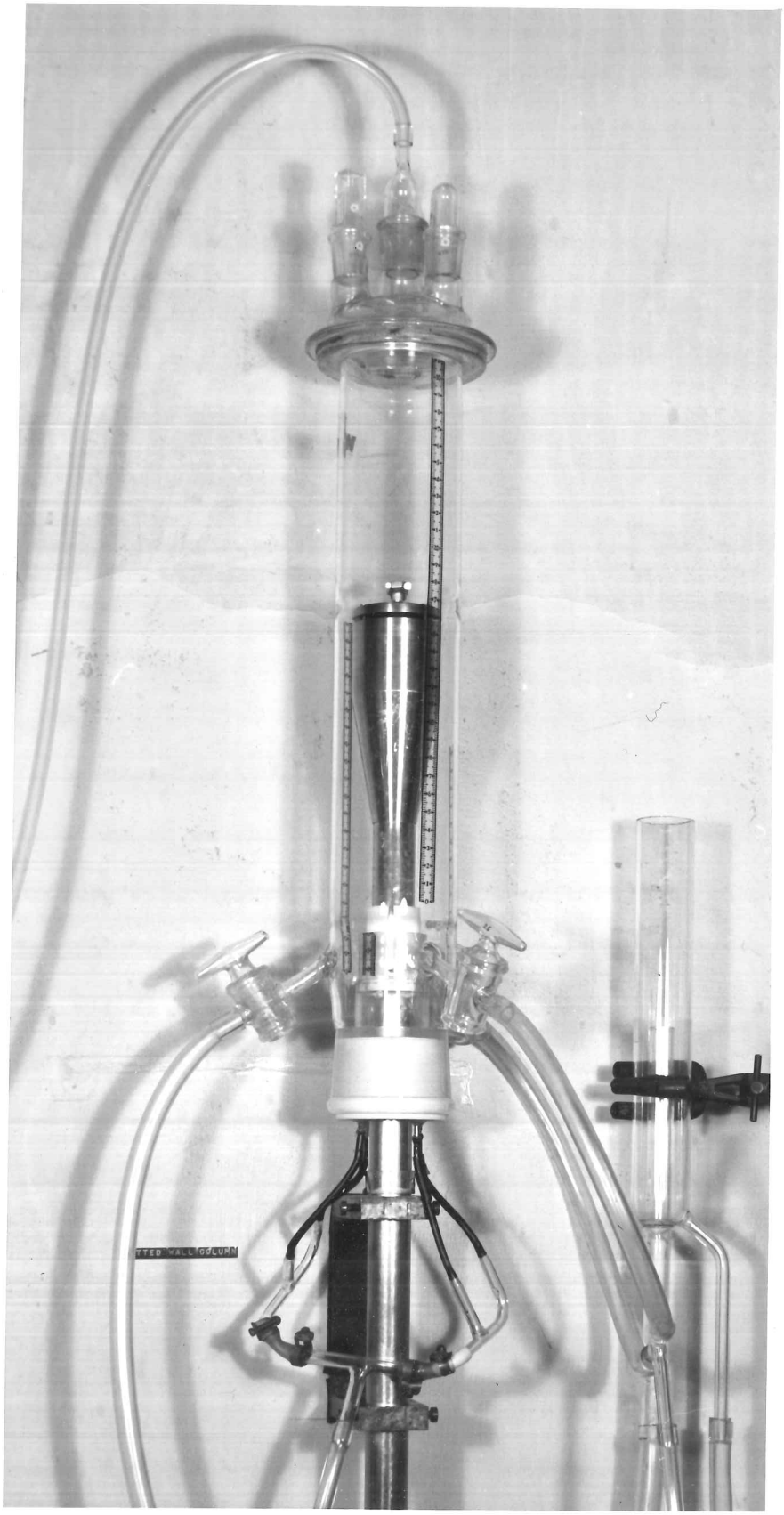

FIG.5-1 THE WETTED-WALL COLUMN

desorbed to monitor the values of k_L. The auxiliary apparatus was similar to that described previously for the packed column and the stirred cell, and gas and liquid samples were taken as previously described to measure the values of k_L and k_G. Distilled deaerated water was used to prepare the desired solutions. In these experiments the peristaltic micropump was not used, and accurately prepared aqueous solutions of acetone, also containing dissolved CO_2, were stored in the main liquid reservoir.

The contact-time for an element of liquid at the surface in the wetted-wall column can (in the unperturbed state) be varied by changing either the height of the exposed film for a fixed liquid flow rate or by changing the liquid flow rate itself. However, a change in the liquid flow rate is accompanied by a change in the thickness of the liquid film, and possibly a change in the entrance effect. Hence it was decided to vary the exposure-time by varying the height of the film. Experimentally, the variation in the enhancement of k_L as a result of a change in the exposure-time was determined. The exposure-time was calculated by dividing the height of the exposed film by the surface velocity of the liquid film. The expression for calculating the surface velocity is available in the literature [D2]. In the absence of Marangoni convection, the mass transfer penetration depth of the solute in the liquid is very small and the velocity gradient equal to zero at the surface, so that velocity changes within the liquid-film can be neglected, and the mass transfer process is adequately described by Higbie's penetration theory. Hence, the average value of the liquid-phase mass-transfer coefficient for an exposure-time θ is given by

$$k_L^* = 2\sqrt{\frac{D_L}{\pi\theta}} \qquad (5.1)$$

To obtain information regarding the rate of growth, the liquid-phase enhancement, E_L, was determined as a function of the height of the liquid film, and the average rate of surface renewal was calculated as described in the following section. The height of the exposed film was varied from around 2.0 cm to 6.5 cm, and the liquid flow rate was varied from about 1.5 cm^3/s to 7.5 cm^3/s. The gas (air) flow rate was varied from 110 cm^3/s to 296 cm^3/s. In all the experiments involving the desorption of acetone, however, the gas flow rate was maintained at a constant value of 250 cm^3/s. For very short heights, acceleration effects at the inlet distributor could give rise to a significant end effect. However, the results of preliminary experiments to check the "ideality" of the apparatus were found to be in good agreement with the predictions of penetration theory for heights as short as 2.5 cm. Hence, the entrance end-effect was assumed to be negligible under the conditions of this investigation in the absence of Marangoni instability.

During preliminary experiments with the wetted-wall column it was observed that relative to the area of the exposed film of liquid, the area of the liquid exposed in the liquid take-off device was quite appreciable. It was therefore decided to account for the mass transfer due to the receiver by independent measurements of the rate of mass transfer due to the receiver alone, in the presence as well as in the absence of acetone desorption. This was achieved by sliding the receiver all the way up to the top of the column such that the height of the exposed film was practically zero. Measurements were carried out for all the liquid and gas flow rates investigated, and the data obtained were used to correct for the mass transfer occurring in the receiver. This correction varied from about 10 to 40 per cent for the desorption of CO_2, the latter figure corresponding to the smallest height of film exposed.

5.3 Theoretical Aspects

Mass transfer in the wetted-wall column in the presence of convective instability may be analysed in terms of a modified surface-renewal theory, and an estimate of the average rate of surface renewal obtained therefrom. The theory as originally proposed by Danckwerts [D5] must primarily be modified to account for the fact that there exists an upper bound on the value of the exposure-time for the fluid elements. The assumptions involved in the development of the theory, in addition to those in the original derivation, are given below.

1. The overall mass transfer process occurs at steady state.
2. The maximum exposure-time, θ, is given by the ratio of the height of the exposed film, h, to the surface velocity, v_s, the latter velocity being calculated assuming the fluid is in rectilinear laminar flow with a parabolic velocity profile.
3. The rate of surface renewal, s, is uniform over the entire area of the exposed film.
4. The solute concentration driving-force in the liquid is essentially uniform over the entire surface exposed to the gas.

Let $\phi(t)$ be the surface age distribution function such that $\phi(t)dt$ represents the fraction of the exposed area which has been exposed to the gas for a time between t and t + dt. If the upper bound on the exposure time is θ, then it can be shown that

$$\phi(t) = \frac{s \exp(-st)}{(1 - \exp(-s\theta))} \qquad (5.2)$$

If $\Delta C_L (=(C_b - C_i))$ is the concentration difference between the bulk and surface concentration of the solute, the rate of desorption per unit area is given by [D2]

$$\bar{R} = \int_0^\theta \frac{s \exp(-st)}{(1 - \exp(-s\theta))} (\Delta C_L) \sqrt{\frac{D_L}{\pi t}} \, dt \qquad (5.3a)$$

$$\text{i.e. } \bar{R} = \frac{\sqrt{D_L s} \, \text{erf}(s\theta)^{\frac{1}{2}}}{(1 - \exp(-s\theta))} (\Delta C_L) \qquad (5.3b)$$

As $s \to 0$, $\bar{R} \to (\Delta C_L) \, 2\sqrt{\frac{D_L}{\pi\theta}}$ as expected from the penetration theory.

In the absence of any Marangoni convection, the rate of desorption per unit area under identical conditions is given by

$$\bar{R}^* = 2\sqrt{\frac{D_L}{\pi\theta}} (\Delta C_L) \qquad (5.4)$$

Dividing (5.3) by (5.4) we obtain an expression for the liquid-phase enhancement factor in terms of s and θ:

$$E_L = \frac{k_L}{k_L^*} = \frac{\sqrt{\pi}}{2} \frac{\sqrt{s\theta} \, \text{erf}(s\theta)^{\frac{1}{2}}}{(1 - \exp(-s\theta))} \qquad (5.5)$$

As $s\theta \to 0$, $E_L \to 1$; and as $s\theta \to \infty$, $E_L \to \frac{\sqrt{\pi s\theta}}{2}$.

Maroudas and Sawistowski [M1] derived an expression for E_L for a similar situation using a slightly different approach. Although their expression appears quite dissimilar mathematically to Equation 5.5, the values of E_L predicted by their expression, for a given s and θ, are in good agreement with those calculated using Equation 5.5, the maximum deviation being around 10%. Moreover, the limiting values of the two expressions for very small and very large values of s and θ are identical.

Figure 5-2 shows a plot of E_L versus $(s\theta)^{\frac{1}{2}}$ as calculated using Equation 5.5.

Figure 5-2 is used to determine the value of the rate of surface renewal as follows. The value of E_L is obtained experimentally; from Figure 5-2 the corresponding value of $s\theta$ is obtained. Since the contact-time, θ, for a given experiment is known, the value of s can be computed. In the experiments carried out the value of s was in general not uniform over the entire exposed area. However, Equation 5.5 could still be used to obtain an estimate of the average value of the rate of surface renewal, $\bar{s}$, over an exposure-time θ. Furthermore, in the presence of Marangoni instability the bulk concentration was not constant, and equal to that at the inlet, because of the mixing due to the Marangoni convection. The change in the bulk concentration was approximately allowed for by using a logarithmic-mean driving force. It should be noted that, in general, the effective depth to which the motion due to Marangoni instability penetrates cannot be estimated at present, although in the case of thin liquid films, such as those encountered in wetted-wall columns, it may be that the Marangoni convection penetrates the entire bulk of the liquid. Since the maximum change in the concentration of dissolved CO_2 under the conditions investigated was around 25%, the error involved in the above procedure was thought to be small.

5.4 Results and Discussion

In order to check that the wetted-wall column was operating "ideally", CO_2 was desorbed from the liquid into the gas phase. Because of the relatively large gas flow rates employed, the CO_2 concentration in the outlet gas was negligible. The rates of desorption determined experimentally were compared with the values predicted by the penetration theory. Figure 5-3 shows that under the conditions investigated, the

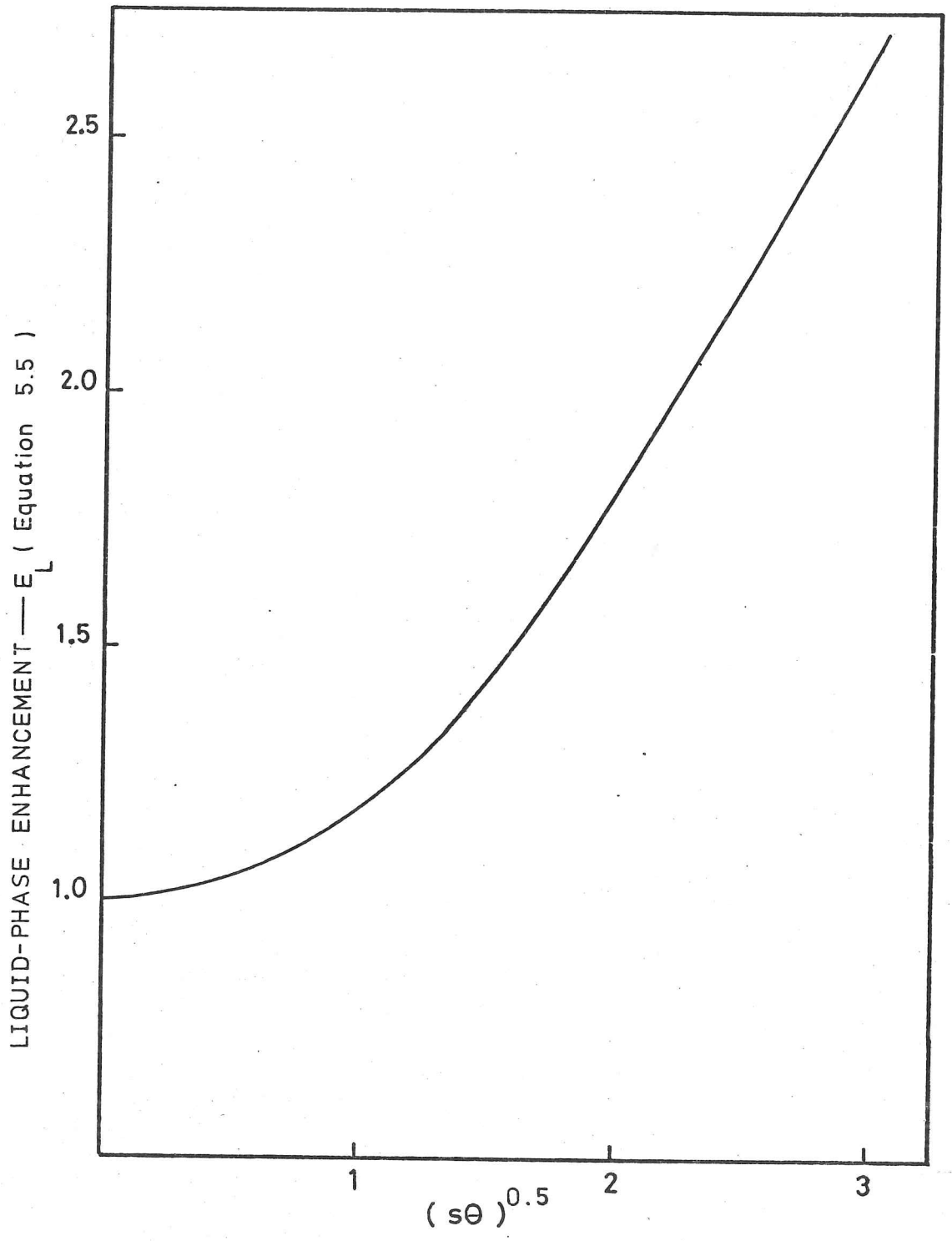

FIG. 5-2 THE LIQUID-PHASE ENHANCEMENT AS A FUCNTION OF $(s\theta)$—AFTER EQUATION 5.5

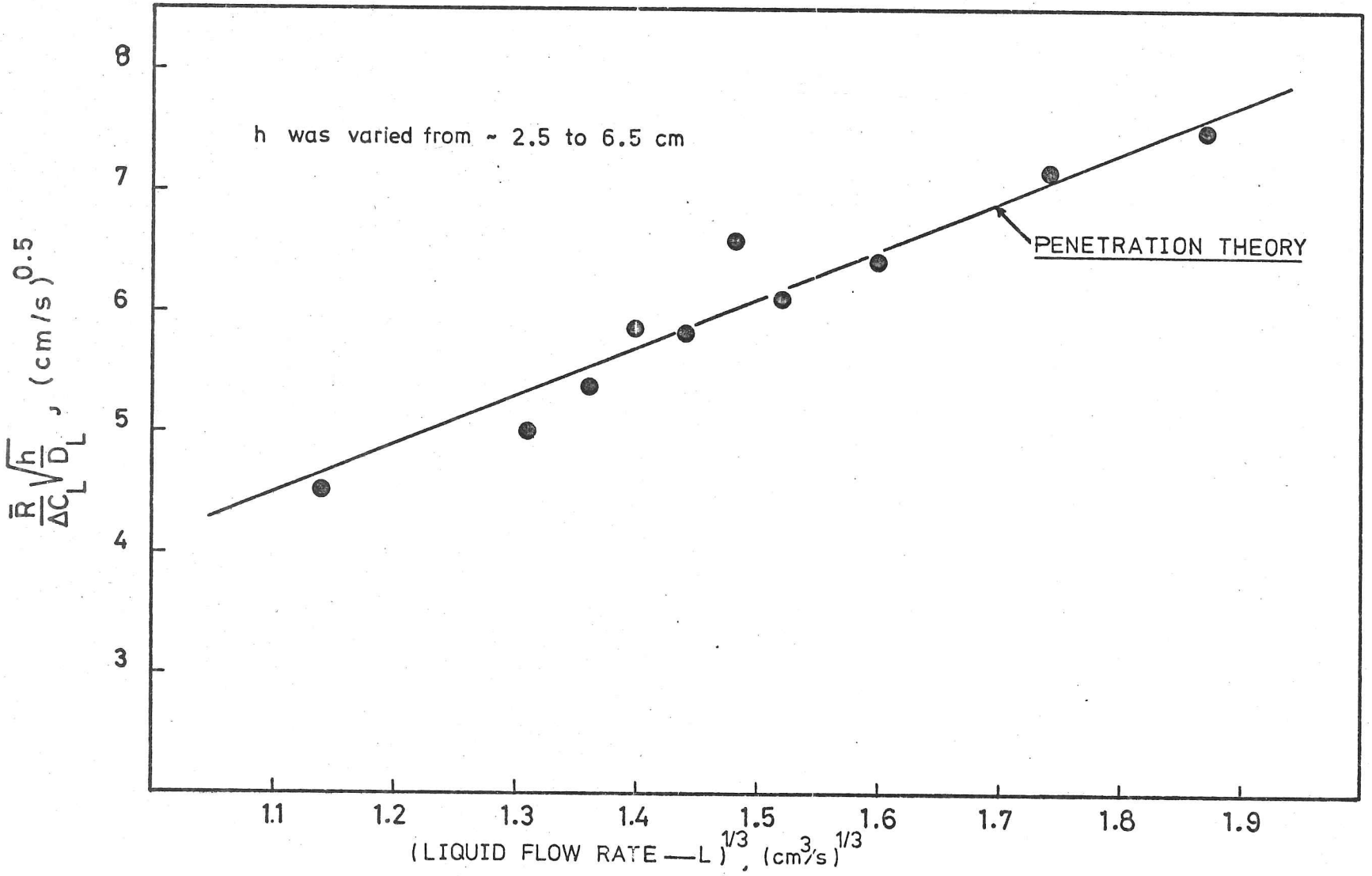

FIG. 5-3 DESORPTION OF CO_2 FROM WATER INTO AIR ON THE WETTED-WALL; 25° C, 1 atm

measured values (corrected for mass transfer due to the receiver) were in good agreement with those predicted theoretically, indicating that in the absence of Marangoni disturbances the apparatus was operating ideally.

Figures 5-4, 5-5, and 5-6 show the enhancement of k_L as a function of the height of the exposed film for liquid flow rates of 3.5, 5.5, and 7.5 cm^3/s, respectively. The acetone concentration was 0.5 wt. %, although for the liquid flow rate of 5.5 cm^3/s some experiments were carried out with an acetone concentration of 0.25 wt. % in the inlet liquid. The figures show that, other things remaining equal, the value of E_L increases with an increase in the height of the liquid film.

Approximate calculations based on the theory of Brian and Ross [B14] indicated that for an acetone concentration of 0.5 wt. %, the liquid was potentially susceptible to Marangoni instability within a couple of milli-seconds of being exposed to the gas phase; in other words, very shortly after leaving the inlet distributor. It can be seen from the plots that as the height of the liquid film tends towards zero, the value of E_L tends towards unity. This result could be anticipated on the basis of Equation 5.5 which states that for a finite rate of surface renewal the value of E_L tends towards unity as the exposure-time tends towards zero. Physically, this corresponds to the case where the exposure-time in the unperturbed state is very much smaller than the reciprocal of the average rate of surface renewal due to the Marangoni instability.

From the plots of E_L versus the height of the exposed film, the average rate of surface renewal was determined, as discussed previously, as a function of the height of the exposed film for a given liquid flow rate and concentration of acetone in the inlet liquid. The values of $\bar{s}$

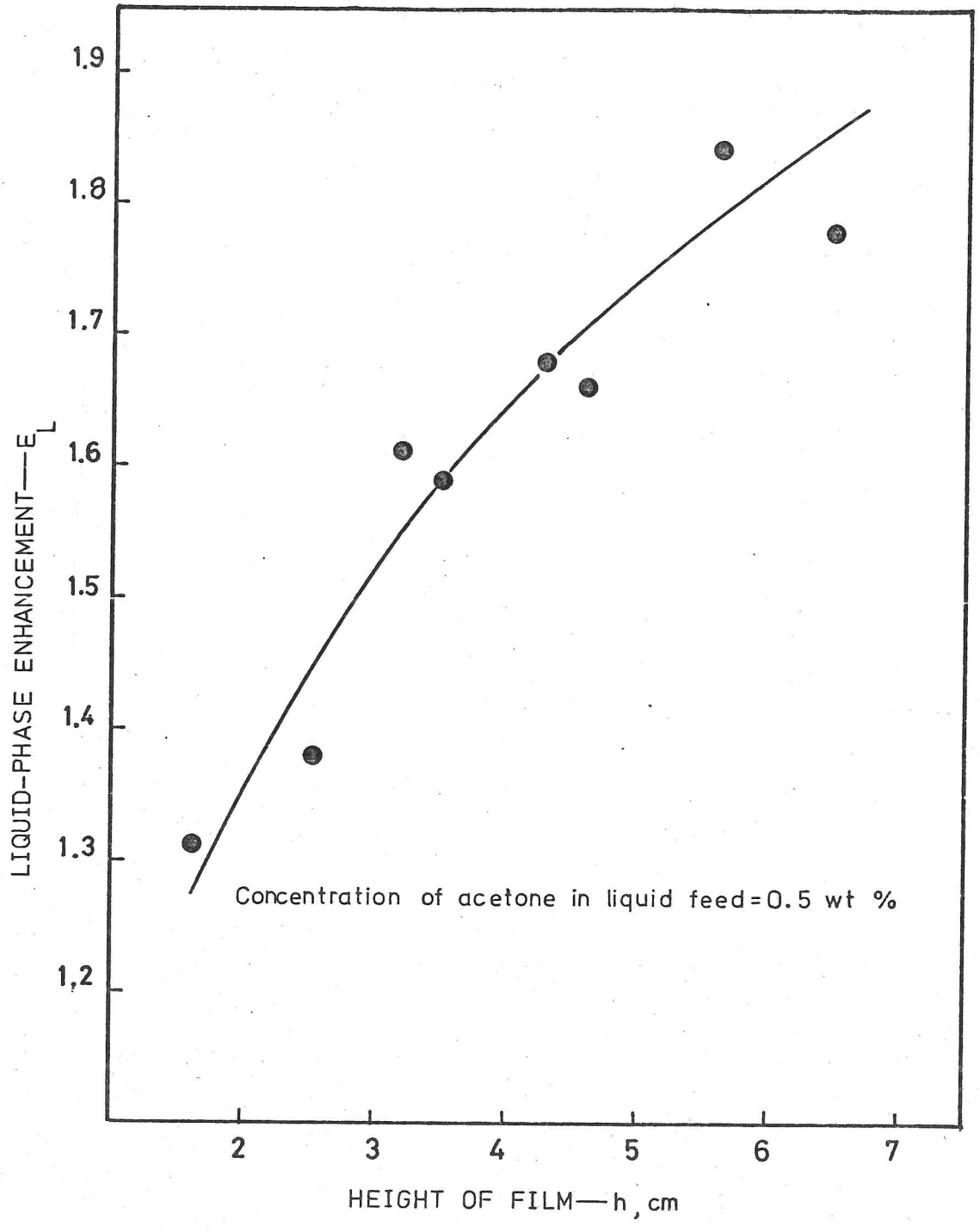

FIG. 5-4 VARIATION OF THE LIQUID-PHASE ENHANCEMENT WITH FILM HEIGHT——WETTED-WALL COLUMN; G=250 cm^3/s, L=3.5 cm^3/s

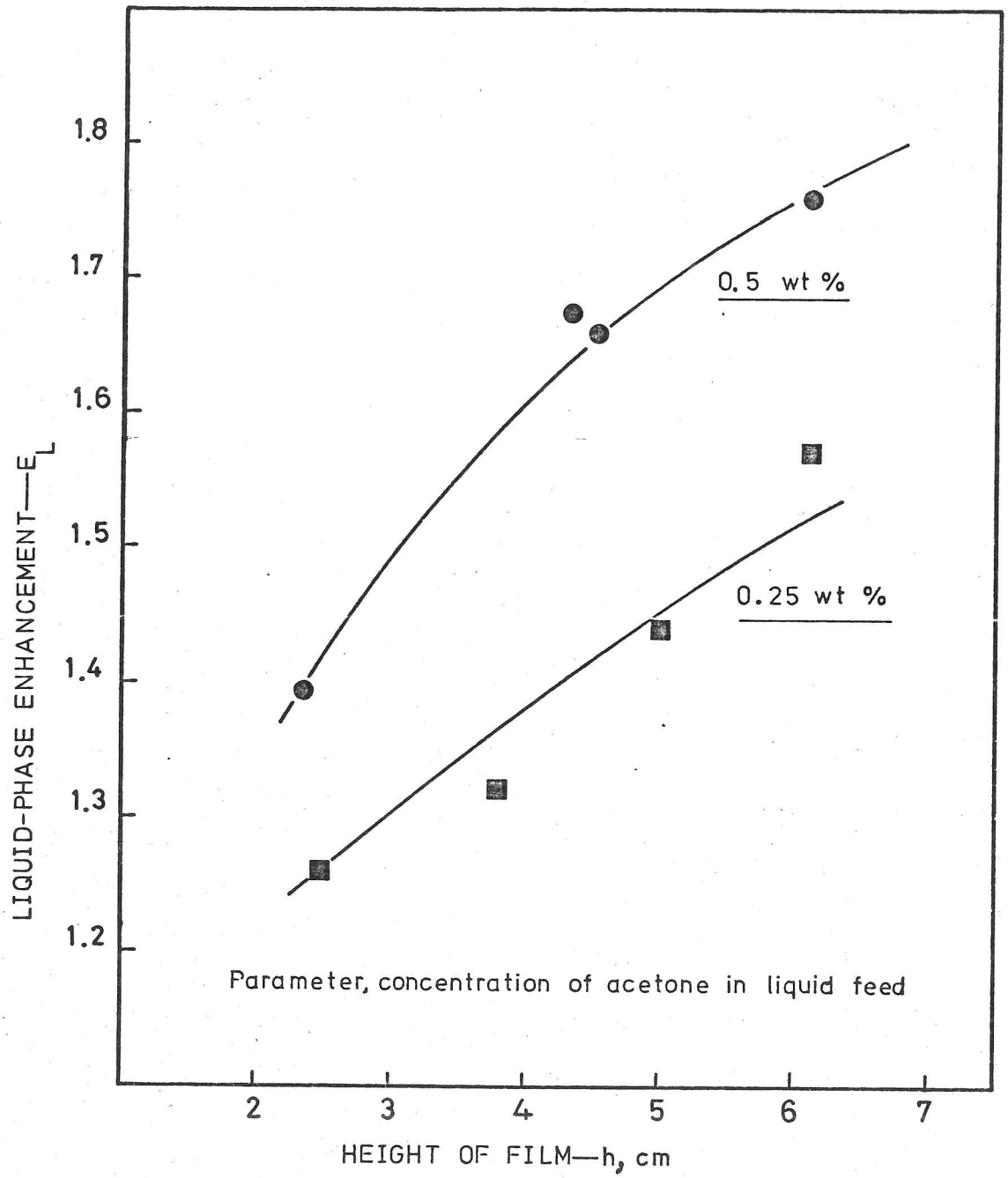

FIG. 5-5 VARIATION OF THE LIQUID-PHASE ENHANCEMENT WITH FILM HEIGHT—WETTED-WALL COLUMN; $G = 250\ cm^3/s$, $L = 5.5\ cm^3/s$

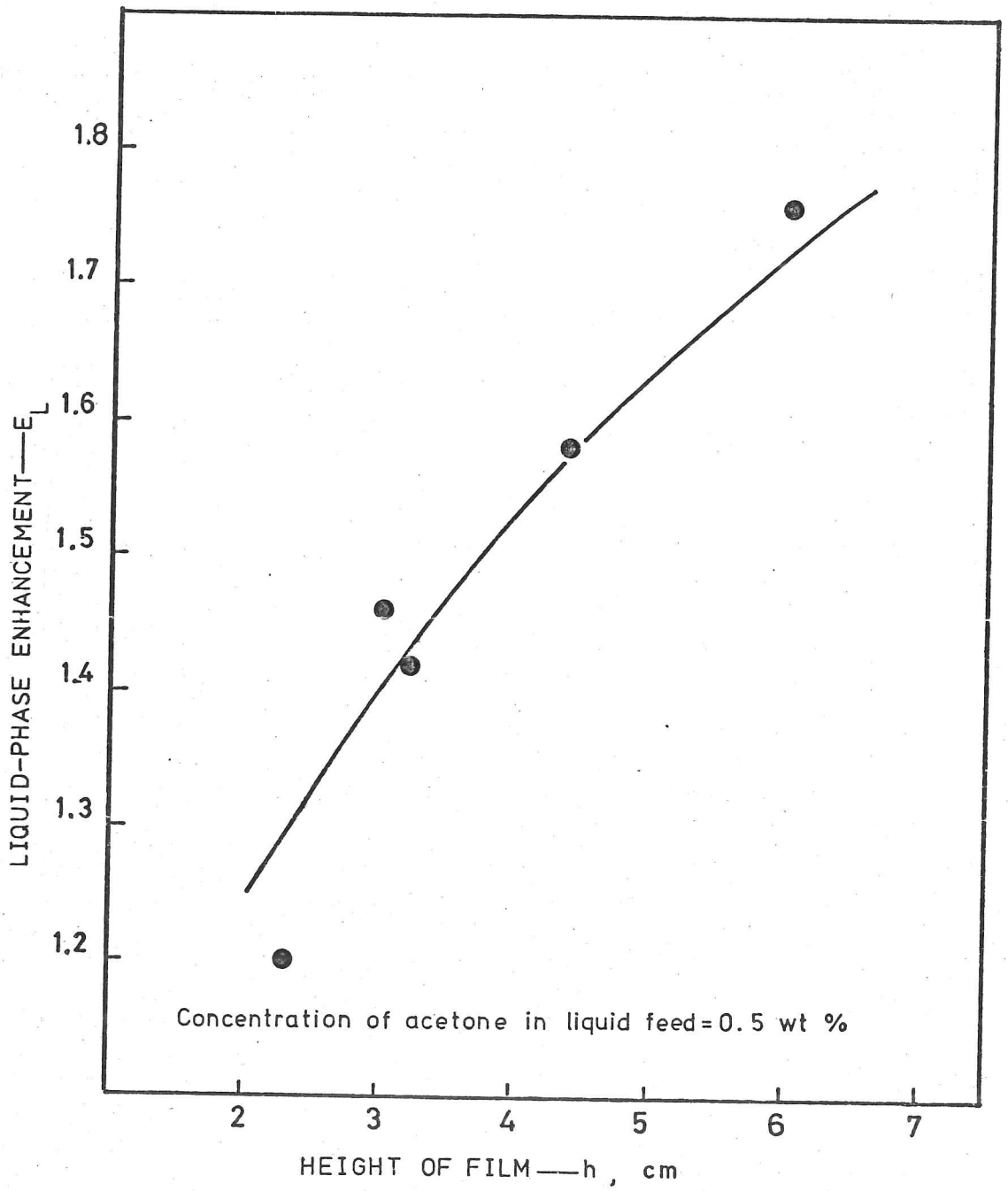

FIG. 5-6 VARIATION OF THE LIQUID-PHASE ENHANCEMENT WITH FILM HEIGHT——WETTED-WALL COLUMN; $G = 250\ cm^3/s$, $L = 7.5\ cm^3/s$

thus obtained are plotted against the film height in Figures 5-7 and 5-8.

The plots show an unexpected trend in that the values of $\bar{s}$ calculated were found to increase with a decrease in the height of the liquid film, i.e. with a decrease in the exposure-time. If growth effects were significant under the conditions investigated, the intensity of the convective motion due to the instability would be expected to increase, at least initially, with time. The value of $\bar{s}$ was also found in general to increase with an increase in the liquid flow rate, other things being held constant. It should be emphasized that the procedure for obtaining the values of $\bar{s}$ from the experimentally determined values of E_L is subject to the assumptions implicit in the theoretical analysis.

An important conclusion which can be deduced, however, is that the rate of growth of the instability was apparently so rapid that, even for relatively very short exposure times, the convective motion due to the Marangoni effect appeared to be fully developed. In other words, the rate of growth of the initial disturbances was rapid enough for the ensuing motion to become fully developed, for all practical purposes, immediately subsequent to initiation, and that relative to the height of the exposed film the region where the initial perturbations were amplified to the point at which they exerted their maximum effect was negligible. Only for the highest liquid flow rate of 7.5 cm^3/s and for small exposed heights of the film did the effect of a finite rate of growth appear to be manifested. This is seen in Figure 5-7 as a decrease in the value of $\bar{s}$ as the height of the exposed film is decreased from 3 to 2 cm.

Measurements of the values of k_G as a function of the liquid flow rate and the height of the film offered some insight as to a probable

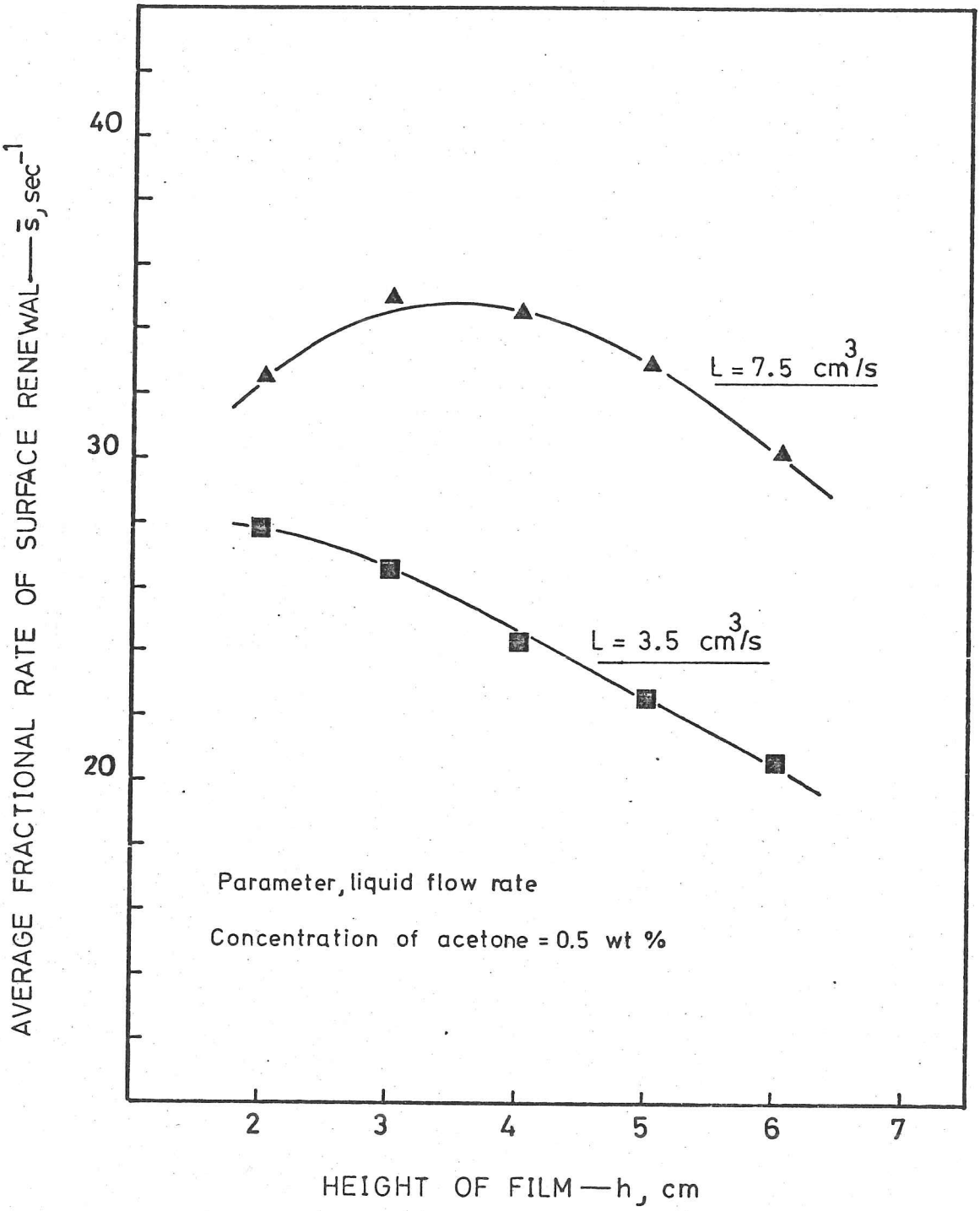

FIG. 5-7 THE AVERAGE FRACTIONAL RATE OF SURFACE RENEWAL AS A FUNCTION OF THE HEIGHT OF THE LIQUID FILM—WETTED-WALL COLUMN ; G = 250 cm^3/s

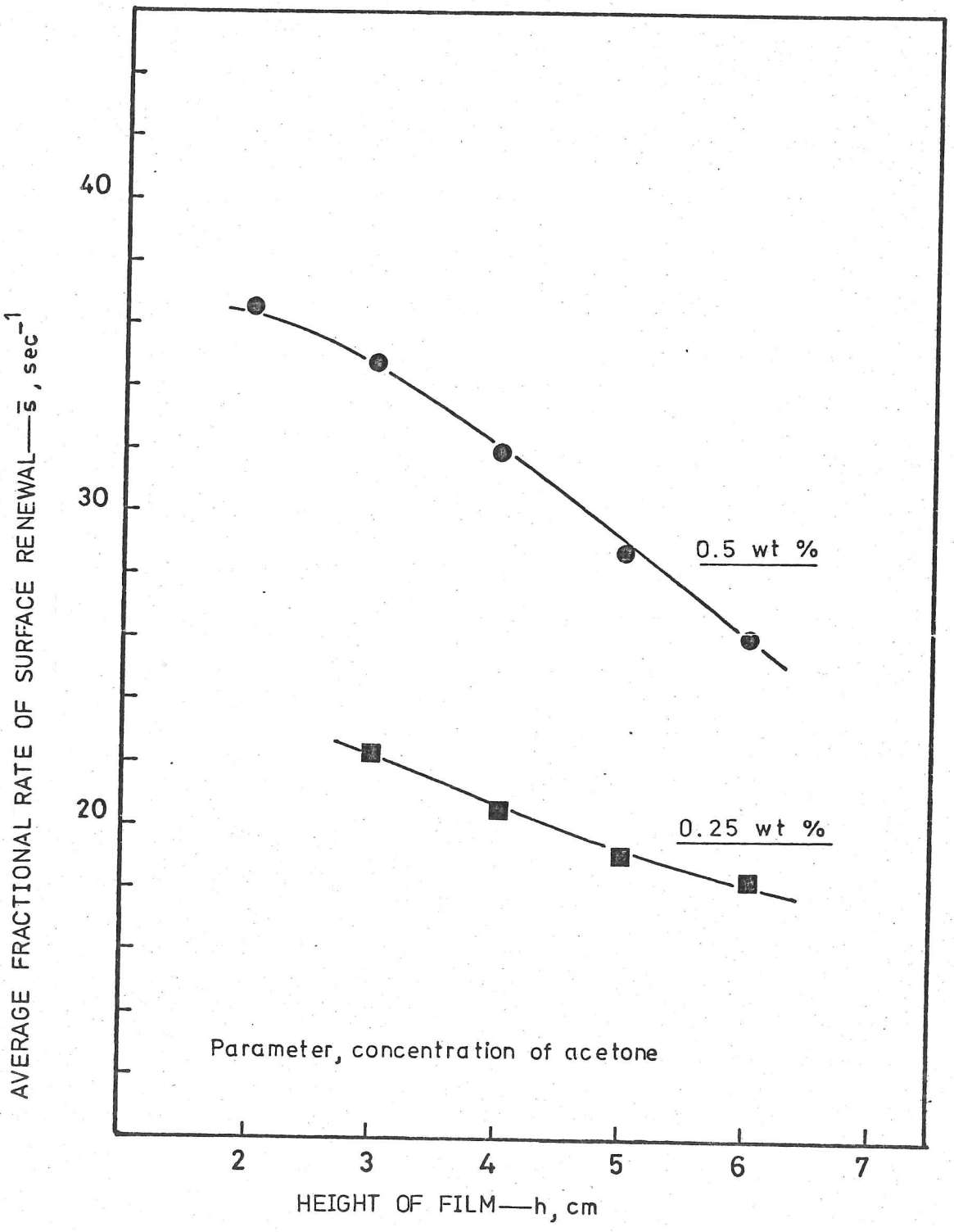

FIG. 5-8 THE AVERAGE FRACTIONAL RATE OF SURFACE RENEWAL AS A FUNCTION OF THE HEIGHT OF THE LIQUID FILM—WETTED WALL-COLUMN; G = 250 cm^3/s, L = 5.5 cm^3/s

cause for the observed increase in the value of $\bar{s}$ with a decrease in the film height. Acetone was desorbed from 0.5 wt. % aqueous solutions into acetone-free air, and the concentration of acetone in the outlet gas stream was measured in the usual manner to obtain the values of the overall gas-phase transfer coefficient. From the latter, the values of k_G were obtained after correcting for the small liquid-phase resistance. In calculating the overall coefficient, the arithmetic average was used in calculating the driving force for acetone desorption. Under the conditions investigated, the maximum concentration of acetone in the outlet gas was about 15 per cent of the saturation value corresponding to the concentration of acetone in the inlet liquid. The gas flow rate was maintained constant at 250 cm^3/s. For the purposes of computing the values of k_G, the interfacial area was taken to be the total area of the liquid exposed to the gas, i.e. including the area in the liquid take-off device.

Figure 5-9 shows the effect of the liquid flow rate and the height of the exposed film on the values of k_G. It is seen that the value of k_G increases with an increase in the liquid flow rate and a decrease in the height of the film. The results obtained are in good qualitative agreement with the very recently published work of other investigators [A1,H2]. The results show that the average rate of desorption of acetone per unit area increases with either an increase in the liquid flow rate or with a decrease in the height of the film. It seems likely that this increase is responsible, at least in part, for the observed increase in the value of $\bar{s}$. It should be noted that the overall driving force for the desorption of acetone did not vary significantly in all the experiments.

The conclusion that the instability grows very rapidly once

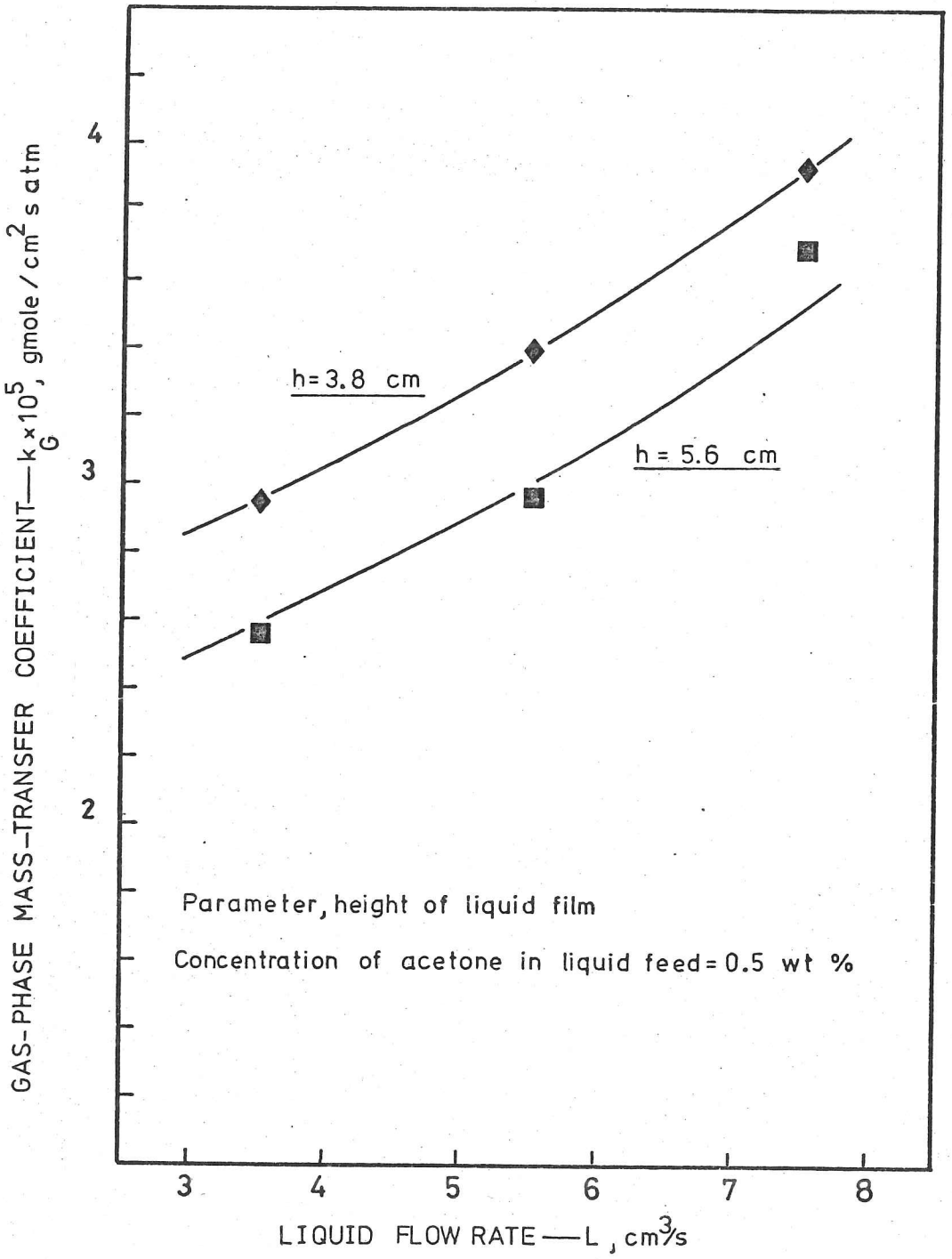

FIG. 5-9 DESORPTION OF ACETONE FROM DILUTE AQUEOUS SOLUTION INTO AIR IN THE WETTED WALL COLUMN; G = 250 cm^3/s ; 25° C, 1 atm

initiated after exposure of a fresh surface in the wetted-wall column should not, in general, be extrapolated indiscriminately to other situations. The liquid film in the wetted-wall apparatus is also subject to hydrodynamic instability which leads to the formation of ripples on the surface of the flowing film. The extent of the interaction of this instability with the Marangoni effect is not known. There appears to be some evidence that in the presence of Marangoni convection ripples manifest themselves much more quickly, i.e. at relatively shorter heights of the liquid film, than in the absence of any Marangoni effects [M2]. In addition, there occurs extremely rapid acceleration of the fluid elements at the surface of the film on leaving the inlet distributor, and the hydrodynamics of the inlet region is not well understood. It is conceivable that there exist small disturbances in the immediate vicinity of the inlet distributor. In the absence of Marangoni instability these disturbances would be rapidly dissipated due to viscous forces and there would be no measurable effect on the rate of mass transfer. In the presence of Marangoni instability, however, these disturbances, if they exist, may be rapidly amplified and manifested as convective instability. Furthermore, it is well known from the theory of hydrodynamic stability that the shape of the velocity profile of the undisturbed flow has a profound effect on the stability of that flow [B10].

Brian et al. [B11] stated that for flowing liquid films the liquid-phase residence time is of no significance for the disturbance mode which takes the form of stationary "roll-cells" with axes aligned in the direction of flow. Apparently, this mode is unaffected by the mean flow velocity and cannot propagate in the direction of the flow. However, a consideration of the accepted mechanism of the manifestation of Marangoni instability together with the available experimental

evidence [G2,M2] indicates that the formation of stationary roll cells of the type described above is most unlikely. Viewed normal to the surface, the morphology appears to be generally in the form of polygonal convection cells which are swept along in the direction of the flow.

5.5 Conclusions and Significance

The Danckwerts' surface-renewal theory has been adapted to the case of mass transfer in the presence of Marangoni instability in a wetted-wall column, and estimates obtained for the average rate of surface renewal for different heights of the liquid film. The experiments indicated that the rate of growth of the instability was very rapid subsequent to initiation. The experiments, however, were not sufficiently refined to give detailed information about the growth of the initial perturbations; the growth apparently occurred in a very small region adjacent to the inlet distributor.

The intensity of the Marangoni convection was found to increase with a decrease in the height of the liquid film, i.e. the exposure-time. Measurements of the values of k_G showed that the value of k_G increases with a decrease in the film height, and this increase in the value of k_G is thought to be responsible, at least in part, for the increase in the intensity of the convective motion, induced by the desorption of acetone, concomitant with a decrease in the height of the liquid film.

CHAPTER SIX

THE MARANGONI EFFECT INDUCED BY THE ABSORPTION OF CARBON DIOXIDE INTO AQUEOUS SOLUTIONS OF MONOETHANOLAMINE

6.1 Introduction and Scope

In their pioneering paper, Brian et al. [B9] reported the occurrence of Marangoni instability during the absorption of CO_2 into aqueous monoethanolamine (MEA) solutions. The authors had noted that severe discrepancies existed between the theoretically predicted values of the rate of CO_2 absorption and the experimental observations of a number of previous investigators in laminar-jet and wetted-wall column apparatus. The presence of Marangoni instability was demonstrated indirectly by an ingenious technique involving the simultaneous desorption of propylene during the absorption of CO_2 in a short wetted-wall column. They observed that the values of k_L were substantially increased by the CO_2-MEA absorption-reaction process, and proposed that the increase was a consequence of the occurrence of Marangoni instability. However, the possible reasons for the manifestation of Marangoni instability were not considered by Brian et al. in their paper. Danckwerts and da Silva [D1] suggested that the instability could be due to the fact that the products of the second-order reaction between CO_2 and MEA are ions, and hence during the absorption of CO_2 into aqueous MEA solutions the surface tension is, in general, substantially higher relative to the inherent surface tension of the sub-surface liquid, a potentially unstable configuration. Electrolytes increase the surface tension of aqueous solutions, and hence at equilibrium the surface concentration is depressed and the surface tension is not greatly increased. If, however, the electrolyte is continuously produced at the surface its

concentration there will be substantially greater than in the bulk, and a correspondingly substantial increase in the surface tension may result. It would increase with the time of exposure because of the finite rate of reaction between CO_2 and MEA. The carbonation reaction is

$$CO_2 + 2\ HOC_2H_4NH_2 \rightarrow OHC_2H_4NHCOO^- + OHC_2H_4NH_3^+$$

and the value of rate-constant at 25°C is 7600 (1/gmole s) [S6].

On the basis of the above hypothesis, the intensity of the Marangoni convection should in general increase with the rate of production of electrolyte at the surface - i.e. with an increase in either the partial pressure of CO_2 in the gas phase or the concentration of MEA in the liquid. Moreover, for sufficiently small values of the above quantities, the effect of the Marangoni convection should be negligible, and there should be good agreement between the theoretically predicted and the experimentally observed values for the rate of CO_2 absorption. The experimental data of several investigators [B9,F1] appear to be in agreement with the above conclusions.

The chemistry of the reaction between H_2S and MEA in aqueous solutions is similar to the reaction between CO_2 and MEA, and the products of the reaction are ions, too. However, in this case the reaction is virtually instantaneous. It is found that the experimentally measured rates of absorption of H_2S into aqueous solutions of MEA are observed to be in good agreement with the theoretically predicted values [D7]. Because the reaction in this case is virtually instantaneous, the concentration of the products is essentially uniform everywhere at the surface, and does not depend on the exposure time [D2]; hence, gradients of surface tension cannot exist.

There is no information in the literature regarding the occurrence, or otherwise, of the Marangoni effect induced by the absorption of CO_2

into aqueous MEA solutions in gas-liquid contactors representative of those used in industrial practice, such as plate or packed columns. Because of the vast quantity of CO_2 absorbed industrially into aqueous amine solutions, or amine-promoted potash solutions, such information is of great practical significance. It was decided, therefore, to investigate the rate of absorption of CO_2 into aqueous solutions of MEA in a small packed column. In order to obtain some information concerning the rate of growth of the Marangoni instability, some experiments were also carried out in a laminar jet apparatus.

6.2 Apparatus and Procedure

6.2.1 The Laminar Jet Apparatus

The laminar jet apparatus was the same as that used by Joosten and details of the apparatus are available elsewhere in the literature [J1,J2]. The main absorption chamber was water-jacketed, and water at essentially 25°C was continuously circulated through the annular space. The inlet liquid nozzles were constructed as described by Sharma [S6], and subsequently checked for ideality by measuring the rate of absorption of CO_2 into pure water. Only those nozzles for which the measured rate of absorption was within 4% of that predicted by penetration theory were retained for further experiments. The receivers were of standard design [D2]. The length of the laminar jet could be varied by means of spacer-rings inserted between the lid and the main body of the absorption chamber [see Figure 6-1b]. The rate of absorption was measured by means of a soap-film meter. The ancillary apparatus was similar to that described by Danckwerts [D2], and the method of operation was similar to that described by Sharma [S6]. The diameter of the laminar jet was measured by means of a travelling microscope. Under the conditions of

investigation, the change in the diameter over the length of the jet was found to be negligible. The entire assembly was built in a constant temperature room maintained at essentially 25°C, and is shown in Figure 6-1a.

Jets of diameter 0.07, 0.096, and 0.14 cm were used. The liquid flow rate was varied from around 1 cm^3/s to 4.2 cm^3/s, and the length of the laminar jet was varied from around 1 to 6 cm. The concentration of MEA was varied from 0.098 M to 0.42 M. Freshly-distilled water was used to prepare the solutions, and the liquid was thoroughly deaerated prior to use. The viscosities of the solutions used were measured by means of an Ostwald viscometer, and were found to be in good agreement with previously reported data [T2]. For the range of concentrations of MEA investigated, the viscosities of the solutions were not significantly different from that of pure water. In addition, it was assumed that the solubility of CO_2 in the aqueous MEA solutions was the same as that in the pure solvent, water. The monoethanolamine used was of reagent grade.

Data on the diffusivity of MEA in aqueous solutions as a function of concentration are available in the literature [T2]. It was assumed that, at the given temperature, the diffusivity of CO_2 in the liquid was inversely proportional to the viscosity of the liquid.

Some experiments were carried out in order to assess the occurrence, or otherwise, of the Marangoni effect under conditions where the aqueous MEA solution contained in addition a dissolved inert inorganic electrolyte; sodium chloride and sodium sulphate were the electrolytes used. Such information would be useful in assessing the importance of the Marangoni effect in the case of CO_2 absorption into amine-promoted potash solutions which have a high ionic strength. In the solutions

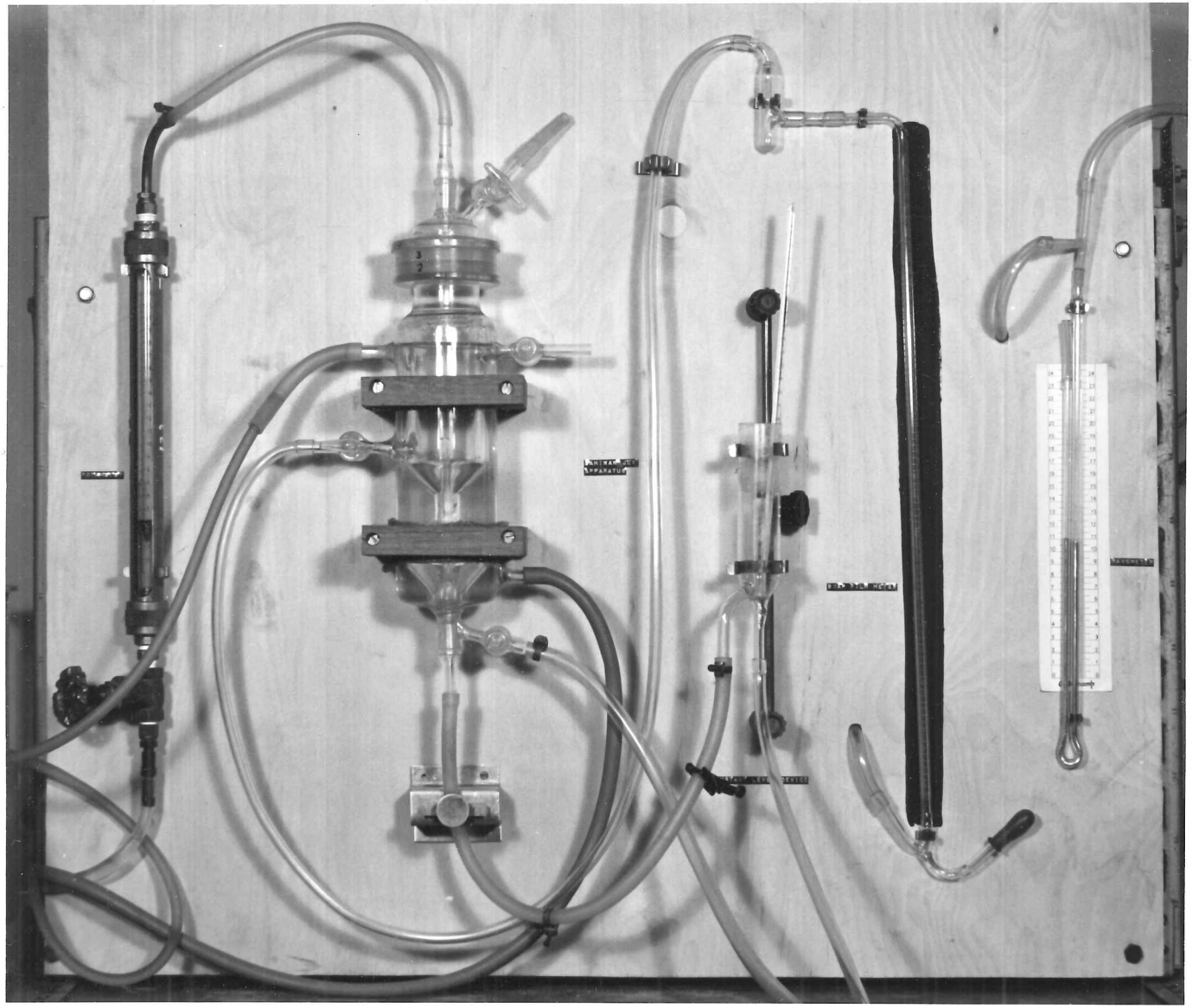

FIG. 6-1a THE EXPERIMENTAL SET-UP FOR THE LAMINAR JET APPARATUS

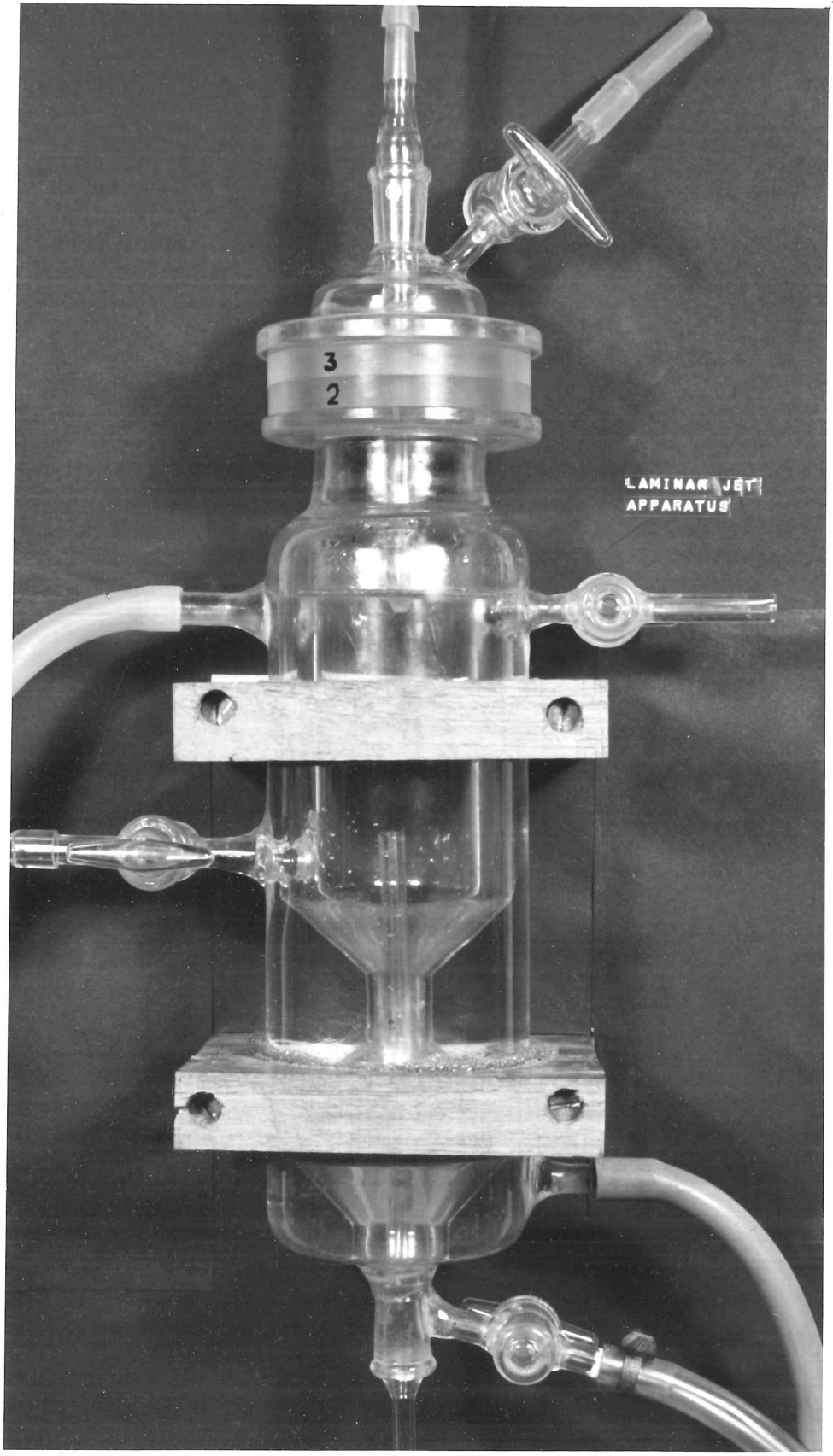

FIG. 6-1b THE LAMINAR JET APPARATUS

containing electrolyte, relatively low concentrations of MEA were used and it was assumed that the change in the physical properties of the liquid phase was due solely to the presence of the inert electrolyte. Data on the diffusivity and the solutiliby of CO_2 in the solutions employed have been reported in the literature [R2]. It was speculated that the presence of the inert electrolyte might influence the occurrence of Marangoni instability through its effect on the changes in surface tension brought about as a result of the generation of ionic products due to the reaction, as well as due to an increase in the inherent surface tension of the bulk liquid, the latter being an inhibitory effect since, in the case of ionic solutions, the surface tension of a freshly-exposed surface is substantially greater than the equilibrium static value.

The contact-time was calculated from a knowledge of the jet height, jet diameter, and the liquid flow rate assuming the jet to be in laminar rod-like flow. The contact-time of the liquid elements was varied by varying the height of the liquid jet and/or the liquid flow rate.

6.2.2 The Packed Column

The packed column was the same as that described in Chapter 3. Porcelain Raschig rings of nominal size 0.64 cm were used, and the effective packed height was 10 cm. The rate of absorption of pure humidified CO_2, at atmospheric pressure, into aqueous solutions of MEA was measured. The CO_2 was passed through the column, countercurrent to the liquid, at a very low flow rate. The rate of absorption was determined from the measurements of the inlet and outlet flow rates by means of soap-film meters. The apparatus was constructed in a constant-temperature room maintained at approximately 25°C. The concentration of MEA in the

inlet liquid was varied from about 0.15 M to 0.51 M. The liquid superficial velocity was varied from 0.18 to 0.58 cm/s. The values of the volumetric liquid-side mass-transfer coefficient for physical absorption of CO_2 into water, $(k_L\underline{a})^*$, had been previously determined (Figure 3-2).

The enhancement E_R $(= \frac{\overline{Ra}}{(k_L\underline{a})^*C_i})$ during the absorption of CO_2 into aqueous solutions of MEA, as determined experimentally, was compared with the theoretical predictions of the surface-renewal models for gas absorption accompanied by a second-order chemical reaction. The theoretical predictions are based on the assumption that the absorption-reaction process has no effect on the hydrodynamics of the liquid phase. The relevant theory has been discussed by Danckwerts [D2]. In the case of the theoretical calculations, based on the average exposure-time of the liquid elements during the physical absorption of CO_2 into water, the reaction between CO_2 and MEA, under the conditions studied, could be considered to be practically irreversible and virtually instantaneous. The concentration of MEA in the outlet liquid was appreciably less than that in the feed; the effective MEA concentration was taken to be the mean of the inlet and outlet values. In order to correct for the effect of the slight change in the viscosity of the liquid due to the presence of MEA, it was assumed that for the packed column $k_L\underline{a} \propto \mu_L^{-\frac{2}{3}}$ [S6]. The ancillary apparatus and the method of operation were similar to that described previously in Chapter 3. As before, freshly-distilled deaerated water was used in the preparation of the desired solutions. The MEA used was of reagent grade.

6.3 Results and Discussion

6.3.1 The Laminar Jet Apparatus

The hydrodynamics of the jets used were checked by measuring the rate

of absorption of CO_2 into laminar jets of water. The data obtained are shown in Figure 6-2, which is a plot of the rate of absorption R' against the square-root of the product of the length of the jet and the liquid flow rate. The value of the slope of the above plot was found to be in good agreement with that predicted by penetration theory for an ideal jet ($= 4C_i\sqrt{D_L}$).

The experimental results in the case of CO_2 absorption into laminar jets of aqueous monoethanolamine are shown in Figures 6-3, 6-4, and 6-5, as a function of the contact-time, for MEA concentrations in the liquid of 0.098 M, 0.18 M, and 0.42 M respectively. For the purposes of comparison, the rates of absorption predicted on the basis of the penetration theory [D2] are also shown in the figures. It can be seen that the experimentally measured rates of gas absorption are substantially greater than the values predicted theoretically over the range of contact-times studied. This discrepancy was attributed to the occurrence of Marangoni instability.

The important result to note is that the instability appears to have manifested itself so quickly that even for contact-times as short as 5 milli-seconds, the ensuing convective motion was of sufficient intensity to enhance the rate of absorption substantially over that predicted theoretically. This implies that the rate of growth of the instability, subsequent to initiation, was very rapid in the case of the laminar jet, and the growth of the instability to the fully-developed state apparently occurred in the immediate vicinity of the inlet nozzle. Figure 6-3 shows that the average flux of CO_2 in the presence of Marangoni disturbances appears to be independent of the diameter of the jet, and is a function only of the exposure-time. Moreover, it is interesting to note that the results obtained appear to be in good agreement with the values predicted

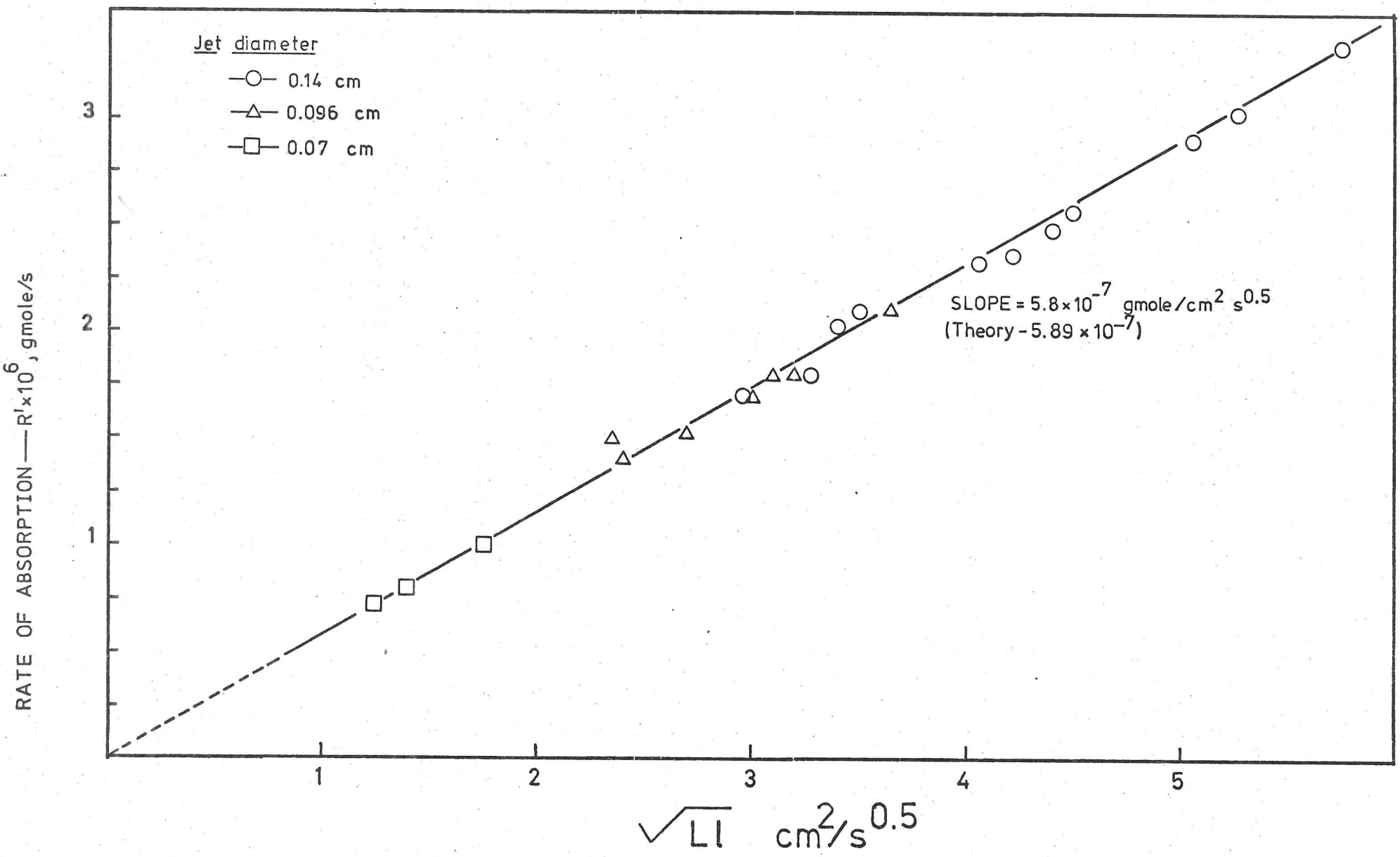

FIG. 6-2 ABSORPTION OF CO_2 INTO WATER—LAMINAR JET; 25° C, 1 atm CO_2

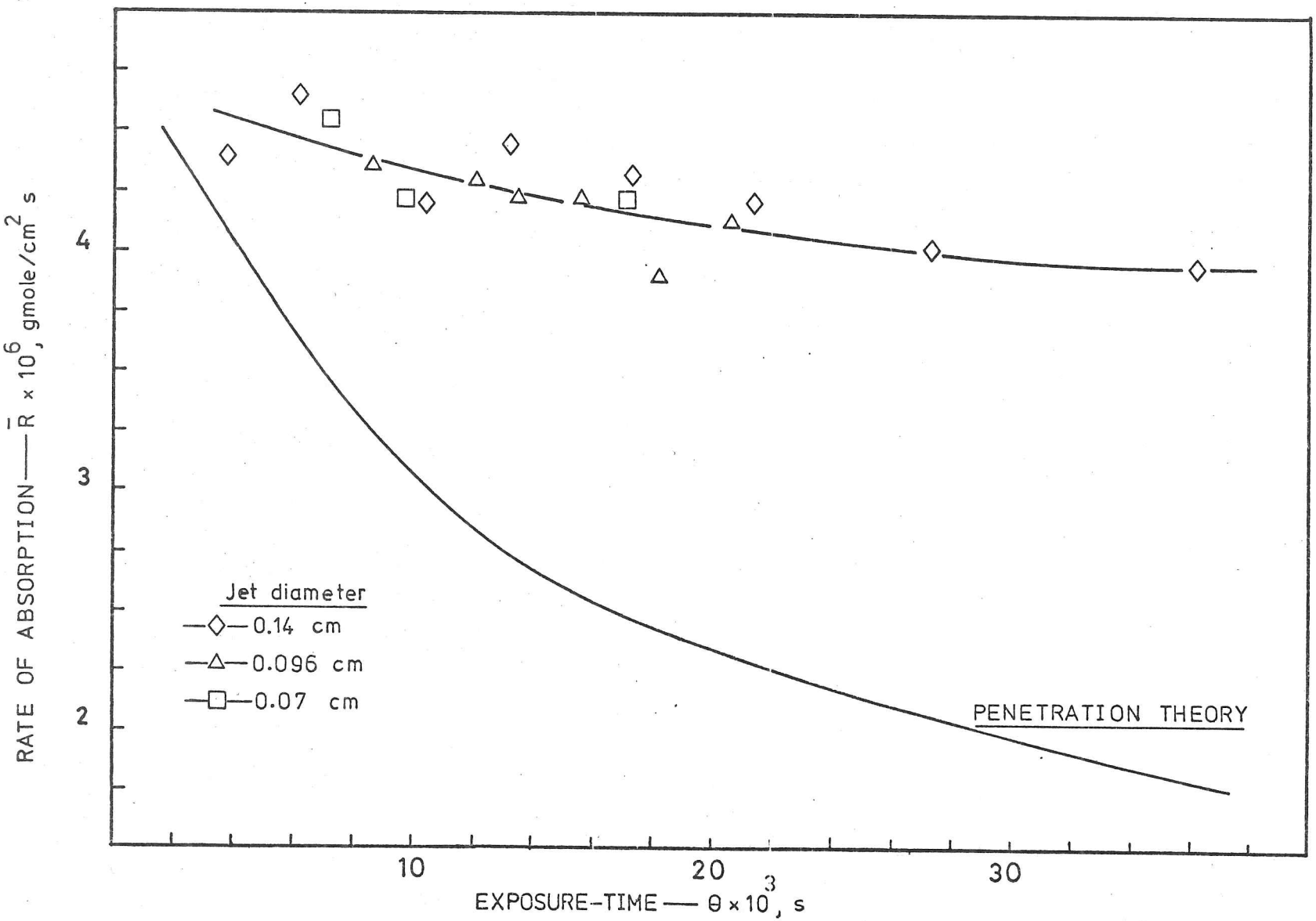

FIG. 6-3 RATE OF ABSORPTION OF CO_2 INTO 0.1 M MEA — LAMINAR JET ; 25° C, 1 atm CO_2

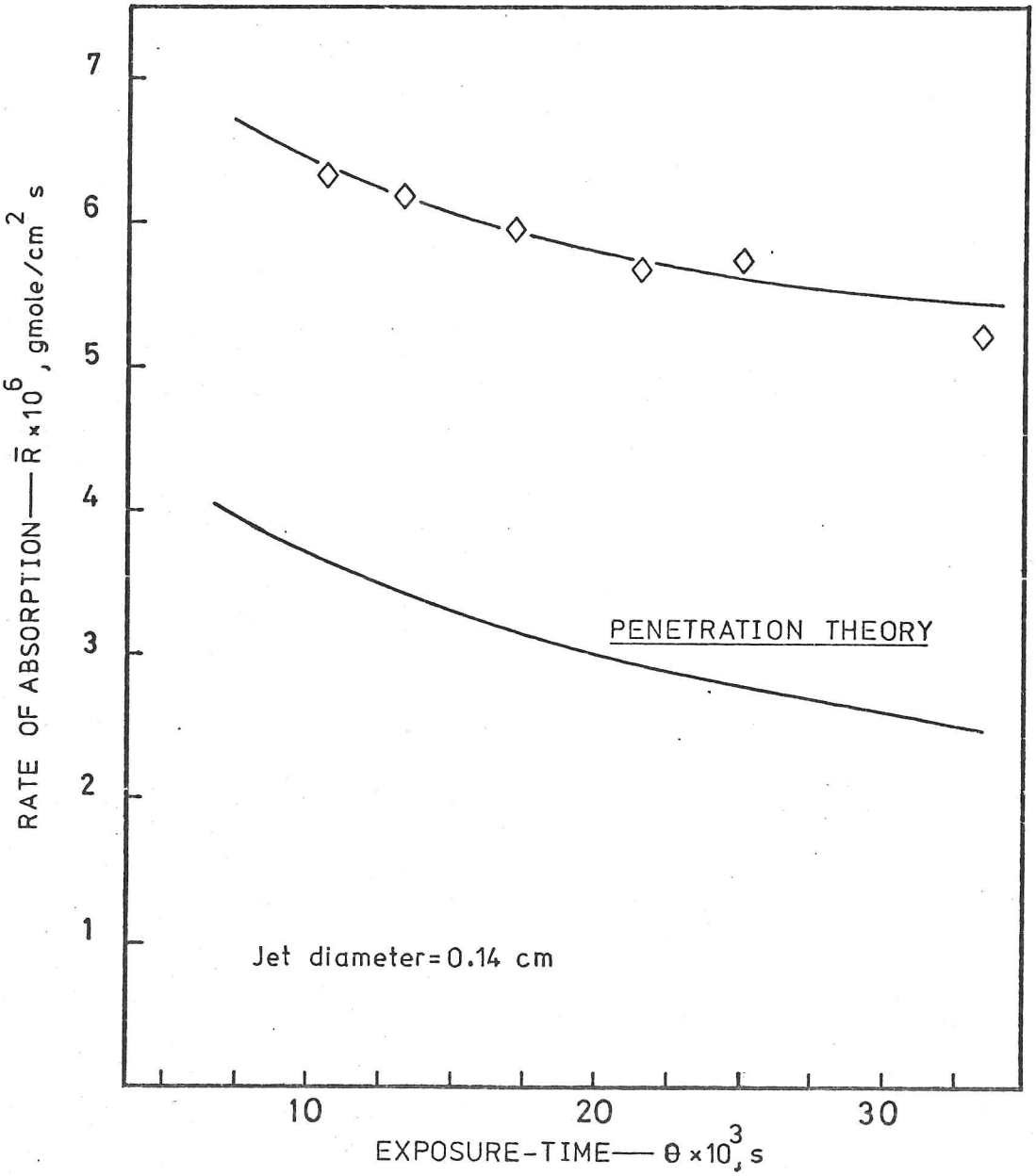

FIG. 6-4 ABSORPTION OF CO_2 INTO 0.18 M MEA — LAMINAR JET; 25° C, 1 atm CO_2

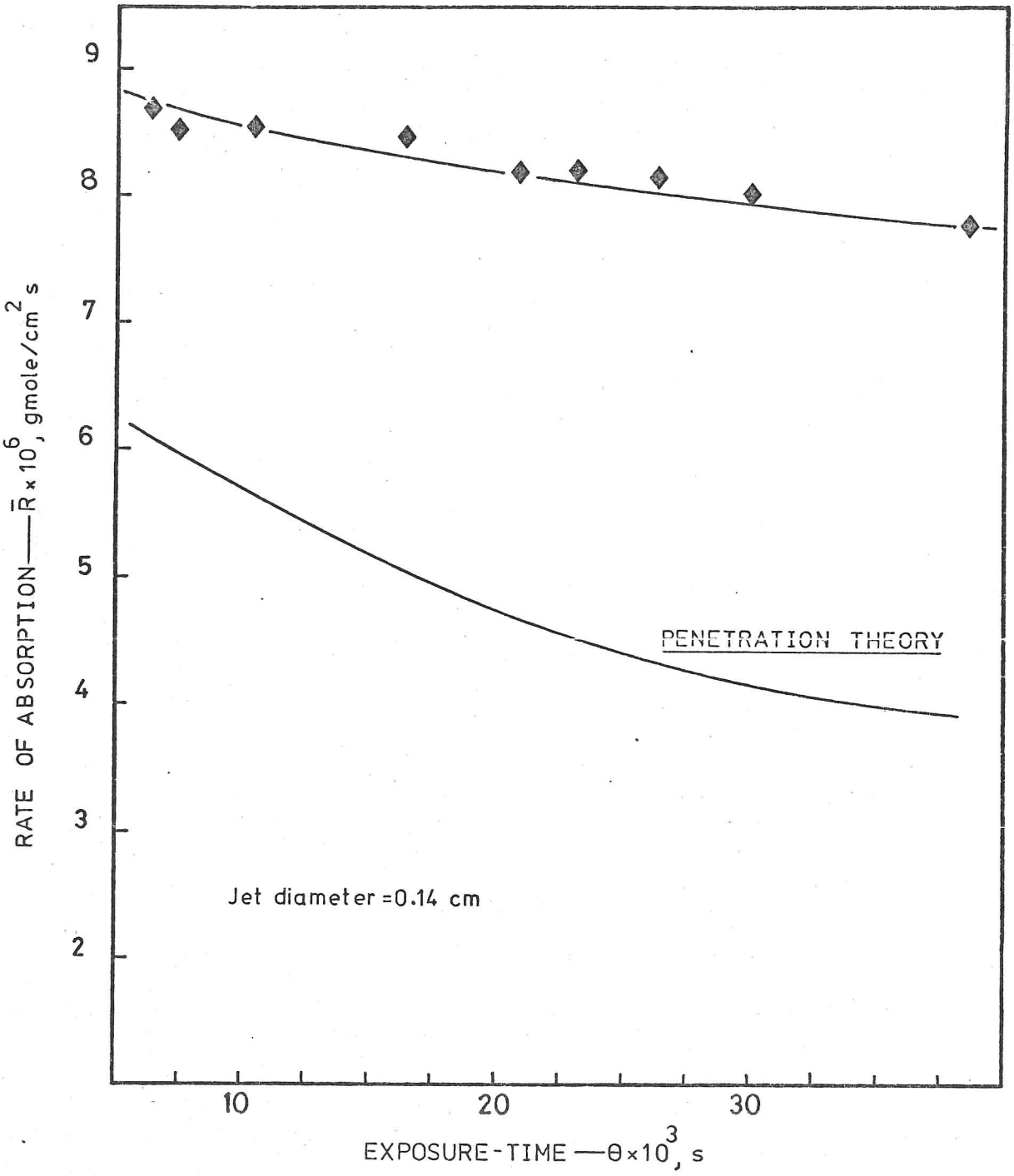

FIG. 6-5 ABSORPTION OF CO_2 INTO 0.42 M MEA—LAMINAR JET; 25° C, 1 atm CO_2

theoretically on the basis of a pseudo-first order reaction, i.e. assuming that there occurs no depletion of MEA in the vicinity of the surface. Due care should be exercised in the interpretation of this result, since the average exposure-time in the presence of Marangoni instability will be less than the exposure-time in the unperturbed state, the latter being the quantity used in the theoretical calculations. It should be noted, however, that in the case where the absorption process is in the fast pseudo-first order regime [see D2 for the relevant criteria], the rate of absorption, as predicted by the penetration theory, is virtually independent of the exposure-time.

Estimates of the increase in the temperature at the surface due to the absorption process showed that the temperature rise at the surface could be neglected under the conditions studied. Methods for estimating the rise in temperature at the surface have been adequately discussed elsewhere in the literature [D2]. It was not possible, however, to obtain estimates of the average rate of surface renewal, as in the case of the wetted-wall column experiments, since the simultaneous desorption of an inert tracer was not carried out to monitor the values of k_L in the presence of Marangoni instability in the case of the experiments with the laminar jet apparatus.

The results of experiments on the rate of absorption of CO_2 into aqueous MEA solutions containing dissolved electrolyte are shown in Figures 6-6 and 6-7. Figure 6-6 shows data for the rate of absorption of CO_2 into a solution containing 0.16 M MEA and 0.88 M NaCl, and Figure 6-7 shows data for the rate of absorption into a solution containing 0.173 M MEA and 0.42 M Na_2SO_4. It is seen that even in the presence of an appreciable amount of dissolved electrolyte, the measured rate of absorption is substantially greater than that predicted theoretically.

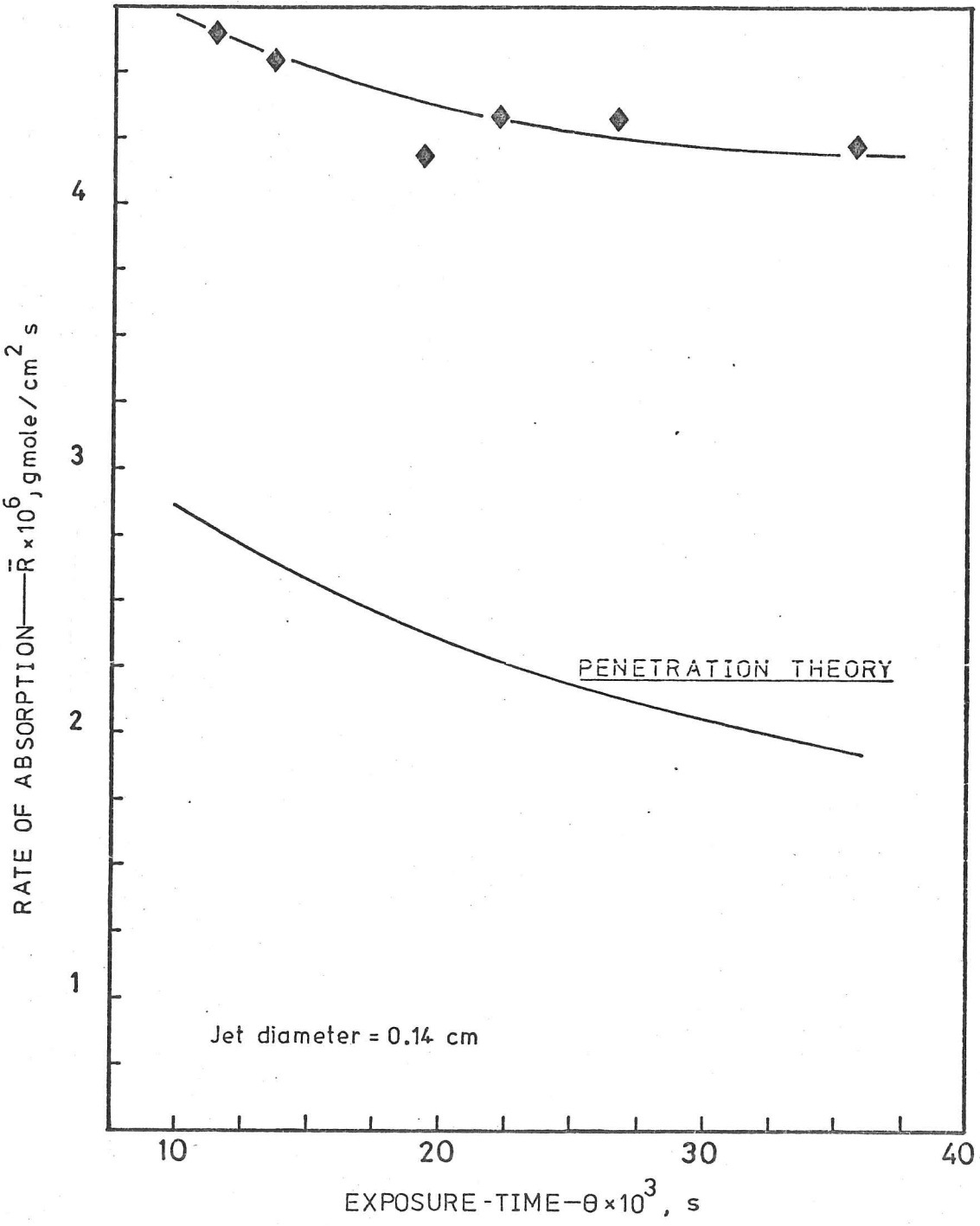

FIG. 6-6 ABSORPTION OF CO_2 INTO AN AQUEOUS SOLUTION CONTAINING 0.16 M MEA AND 0.88 M NaCl—LAMINAR JET; 25° C, 1 atm CO_2

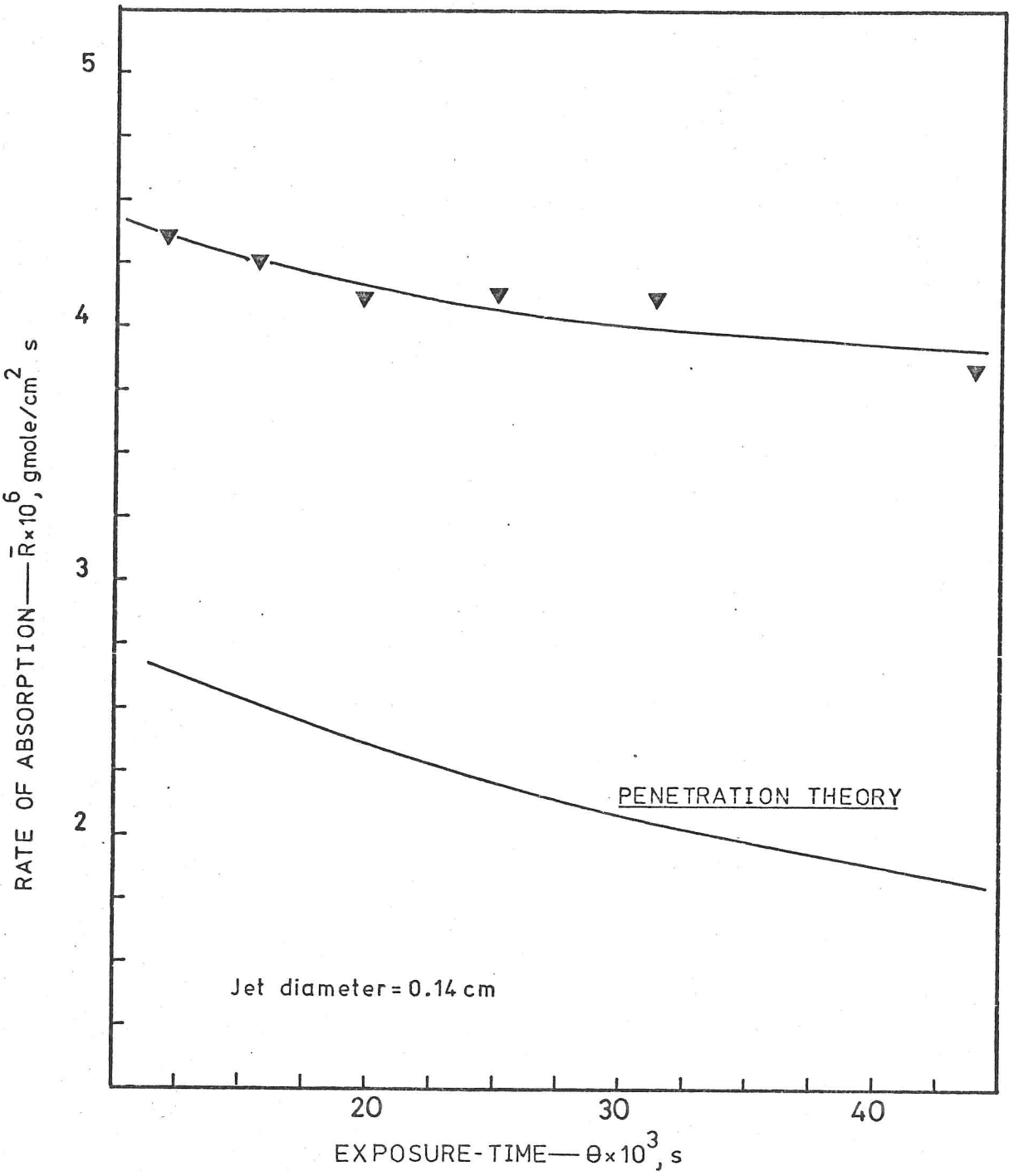

FIG. 6-7 ABSORPTION OF CO_2 INTO AN AQUEOUS SOLUTION CONTAINING 0.173 M MEA AND 0.42 M Na_2SO_4 —— LAMINAR JET; 25° C, 1 atm CO_2

It was assumed, for the purposes of the theoretical calculations, that the presence of the ions did not have any effect on the value of the rate-constant for the reaction between CO_2 and MEA. It was not possible, however, to determine the effect of the ions, if any, on the intensity of the Marangoni convection, other things remaining equal. In this connection it would be interesting to carry out experiments involving the simultaneous desorption of an inert tracer, e.g. nitrous oxide, during the absorption of CO_2 into the aqueous solutions of MEA.

In the course of writing this dissertation, Sada et al. [S11] reported data for the absorption of CO_2 into laminar jets of aqueous solutions of MEA under conditions similar to those employed in this work. Their data are in good agreement with the conclusions reported in this investigation. Moreover, Sada et al. used ethylene as an inert tracer to monitor the values of k_L during the absorption of CO_2. Hence, their data can be used to obtain estimates of the average rate of surface renewal, using the theory developed in the previous chapter. For example, they found that for an exposure-time of 15×10^{-3} seconds, the value of E_L was equal to 1.9 and 3.2 during the absorption of CO_2 into 0.1 M and 0.463 M MEA, respectively. Using Equation 5.5, the estimated value of $\bar{s}$ for the case of absorption into 0.1 M MEA is 294 s^{-1}, while that for the case of absorption into 0.463 M MEA is 867 s^{-1}. The estimated values indicate vigorous convective motion due to the Marangoni instability.

6.3.2 The Packed Column

The results of experiments on the rate of absorption of CO_2 into aqueous solutions of MEA in the packed column are shown in Figure 6-8. The figure shows that the experimentally measured rates of CO_2 absorption are in good agreement with those predicted on the basis of the surface-renewal models [D2] and the measured values of $(k_L a)^*$ for physical

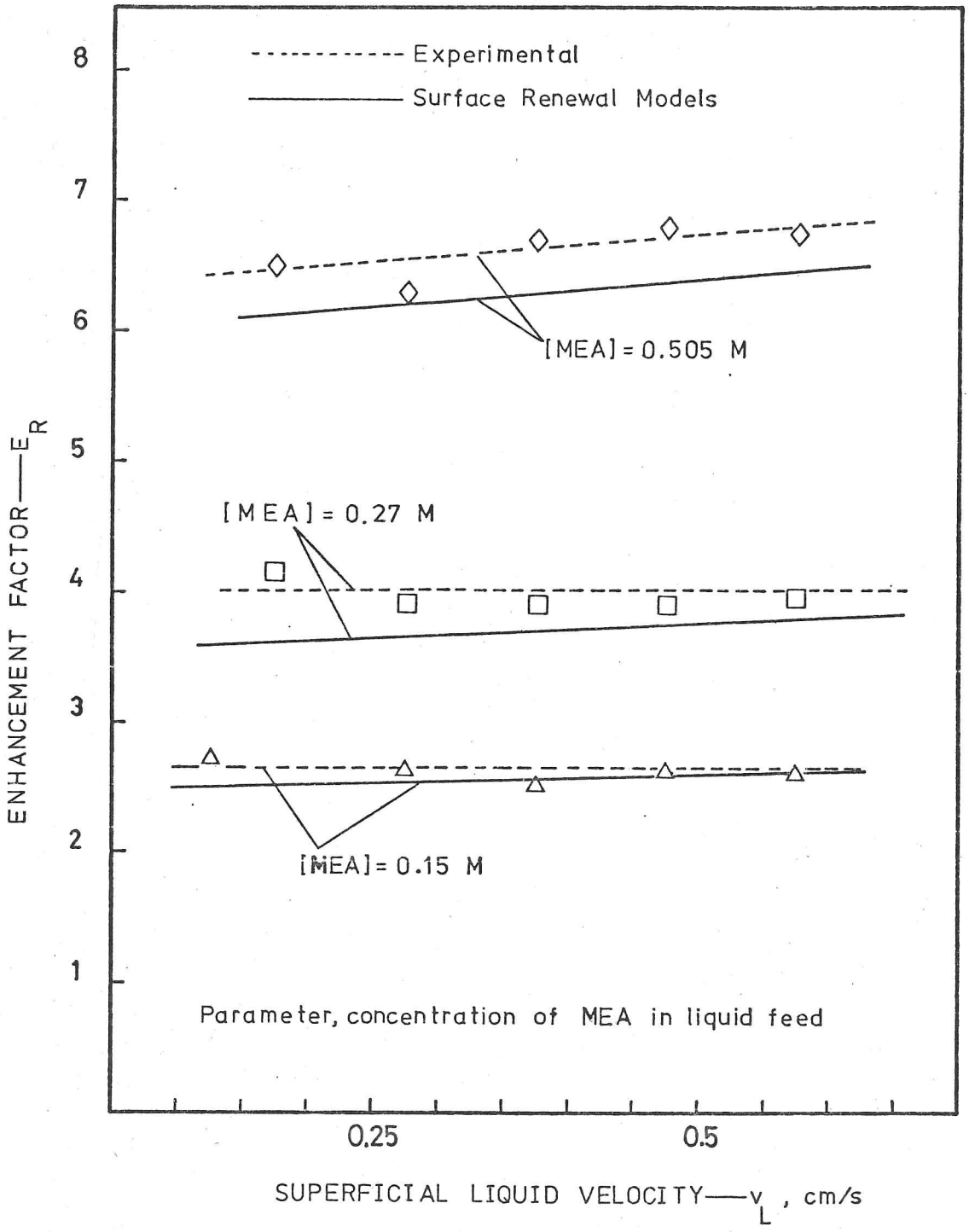

FIG. 6-8 ABSORPTION OF CO_2 INTO AQUEOUS MEA SOLUTIONS—PACKED COLUMN; 0.64 cm RASCHIG RINGS; 25° C, 1 atm CO_2

absorption in the packed column.

The fact that during the absorption of CO_2 into aqueous MEA solutions in the packed column there is apparently no evidence of Marangoni instability is very puzzling when one takes into account the enhancement of the rate of absorption observed in laminar jet apparatus and in short wetted-wall columns for similar values of the concentration of MEA in the liquid and much shorter exposure-times of the liquid elements.

The precise explanation for the apparent absence of the Marangoni effect during absorption in the packed column is not known. However, the factors discussed below might account, at least in part, for the observed anomaly. One possible cause could be the accumulation of 'contaminants' at the surface of the flowing liquid in the packed column, thereby suppressing Marangoni convection. In the experimental set-up employed, the liquid from the packing was drained without discontinuity into a pool of liquid, the level of which was maintained constant, thus allowing for the possibility of a build-up of a contaminant film. It should be noted that the build-up of a contaminant film would be aided by any initial convective motion prior to suppression. Alternatively, the observed anomaly could be due to the difference in the hydrodynamics of the unperturbed liquid flow in the packed column relative to that in laminar liquid jets on wetted-wall columns. This difference in the hydrodynamics of the unperturbed flow may affect not only the conditions for the occurrence of Marangoni instability, but also the rate of growth of the instability. It may be that in the packed column the reaction could be considered as effectively instantaneous (no surface-tension gradients possible) for an exposure-time much smaller than the time required for the Marangoni effect to manifest itself assuming the reaction to be pseudo-first order. It should be noted that even in the case of

desorption of acetone from aqueous solutions (Chapter 3), the enhancement of $k_L a$ in the packed column was much smaller than that anticipated by extrapolation of data obtained in wetted-wall columns [B11, Chapter 5].

6.4 Conclusions and Significance

The experiments in the laminar jet apparatus showed that the rate of growth of Marangoni instability therein, induced by the absorption of CO_2 into aqueous MEA solutions, was fast enough for the ensuing Marangoni convection to have a significant effect on the rate of absorption of CO_2 for an exposure-time of around 5 milli-seconds or more. In view of the above result, the apparent absence of Marangoni convection in the case of the packed column was a surprising and unexpected result. Because of the many and diverse factors which influence the occurrence of Marangoni convection, the reasons for the anomalous result in the packed column are not easily deduced. The experiments, however, showed that given the current state of knowledge on the subject, it would be reckless to extrapolate data obtained under one set of hydrodynamic conditions to a completely different set of hydrodynamic conditions.

CHAPTER SEVEN

MISCELLANEOUS ASPECTS

A: THE THEORETICAL PREDICTION OF THE EFFECT OF MARANGONI CONVECTION ON THE RATE OF INTERFACIAL MASS TRANSFER

7A.1 Introduction and Scope

There is practically no information available in the literature regarding the a priori prediction of the effect of Marangoni convection on the rate of interfacial mass transfer in unstable gas-liquid systems. In addition, the available relevant information is rather fragmentary and deals in general with extremely simplified models. It is likely that the development of predictive mechanistic models has been hampered by the relatively complex and diverse nature of the resulting convective flows. In what follows, an attempt has been made to rationalize and extend the analysis of previous investigators. The analysis will be limited to those cases where the convective flows are relatively ordered, i.e. the "cellular" convection regime [S1,S2]. In addition, only a 2-dimensional model will be analysed. Although a 2-dimensional model is unrealistic from a physical point of view, it represents a convenient basis for the development of more realistic models.

Experiments have shown that under the conditions generally encountered, the Marangoni convection has no influence on the mass-transfer coefficient in the gas phase. Hence, the analysis will be restricted to the enhancement of the mass-transfer coefficient in the liquid phase, and it will be assumed that the gas-phase hydrodynamics can be represented by a constant gas-side mass-transfer coefficient.

7A.2 The Theoretical Model

The model analysed is shown in Figure 7-1. The liquid is assumed to be infinite in lateral extent and initially quiescent. The convective motion arising from the occurrence of Marangoni instability, induced by a destabilising gradient of temperature or concentration, is represented by ordered contrarotating "cellular" convective flows as shown in the figure. For the purposes of this preliminary analysis the following assumptions are made:

1) the instability is fully-developed, and the system is at steady (or quasi-steady) state;

2) the interface is assumed to be planar (horizontal) and inflexible;

3) the liquid is Newtonian and the convection cells are of a uniform size;

4) surface viscosity and elasticity effects (including effects due to the Gibbs adsorption layer, if any) are negligible;

5) the physical properties of the liquid are the same at all points in the liquid phase;

6) the surface tension varies linearly with distance along the surface of each convection cell, i.e. the gradient of surface tension with respect to the distance along the surface, $\frac{\partial \gamma}{\partial x}$, is equal to a constant.

Since the overall mass transfer process can be represented in terms of the transfer from the individual convection cells, further discussion will be limited to the analysis of a single convection cell. Let x_o be the size of the cell (as shown in the figure), and $\Delta\gamma$ be the difference

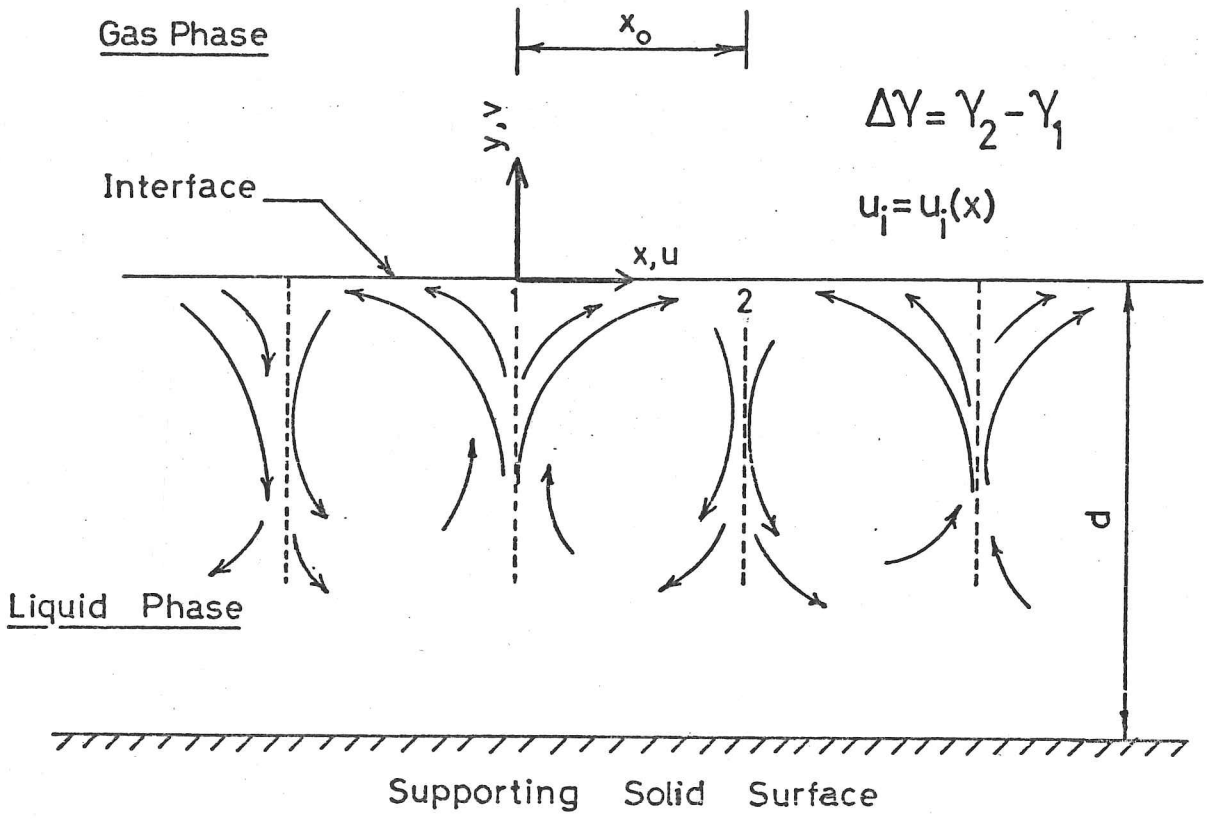

FIG. 7-1 SCHEMATIC DIAGRAM OF THE THEORETICAL MODEL

in the values of the surface tension at the extremities of the cell. Let d be the depth of the liquid phase. The reference co-ordinate axes are as indicated in the figure. Let $u_i(x)$ be the velocity of the liquid at the surface of the cell in the x-direction, i.e. along the surface. Provided that the mass-transfer penetration depth is small, the velocity gradients normal to the surface can be neglected and it can be shown [R5] that the liquid-side mass-transfer coefficient, averaged over the cell, is given by the expression:

$$k_L = 2\sqrt{\frac{D_L}{\pi x_o}}\left[\frac{1}{x_o}\int_o^{x_o} u_i(x)\, dx\right]^{\frac{1}{2}} \qquad (7.1)$$

Hence, to evaluate the value of k_L, $u_i(x)$ must be determined. D_L is the diffusivity of the solute in the liquid phase. The determination of $u_i(x)$ is discussed below with respect to two limiting cases.

Case I: $x_o >> d$

For very thin liquid layers where the above condition is satisfied and neglecting cell-edge effects, it can be shown [L2] that the surface velocity is essentially constant over the width of the cell and is given by

$$u_i = \frac{d(\Delta\gamma)}{4\mu_L x_o} \qquad (7.2)$$

The necessary conditions to be satisfied are

$$d^3 << \frac{4\mu_L{}^2 x_o^2}{\rho_L(\Delta\gamma)} \qquad (7.3)$$

and

$$\frac{u_i d\rho_L}{\mu_L} << 1 \qquad (7.4)$$

where μ_L and ρ_L are the viscosity and density of the liquid phase, respectively. Substituting Equation 7.2 in Equation 7.1 one obtains:

$$k_L = 2\left[\frac{D_L(\Delta\gamma)d}{4\pi\mu_L x_o^2}\right]^{\frac{1}{2}} \tag{7.5}$$

It can be seen from the above expression that in order to estimate the value of k_L, the values of x_o and $(\Delta\gamma)$ must be known or estimated. Alternatively, for a fixed value of x_o the corresponding value of k_L can be determined if the value of $\Delta\gamma$ can be independently estimated.

Case II: $x_o << d$

The complete equation for the velocity component in the x-direction at steady state is (for the 2-dimensional case) [N1]

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho_L}\frac{\partial p}{\partial x} + \nu_L\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \tag{7.6}$$

Since we are interested in the velocity at the surface and because of the preliminary nature of the analysis, the terms $v\frac{\partial u}{\partial y}$, $\frac{1}{\rho_L}\frac{\partial p}{\partial x}$ and $\nu_L\frac{\partial^2 u}{\partial x^2}$ will be assumed to be negligible. Furthermore, the term $u\frac{\partial u}{\partial x}$ will be replaced by $u_i\frac{\partial u}{\partial x}$. It should be noted that cell-edge effects are neglected in this analysis. Thus Equation 7.6 reduces to

$$u_i\frac{\partial u}{\partial x} = \nu_L\frac{\partial^2 u}{\partial y^2} \tag{7.7}$$

The boundary conditions are:

i) at $x = 0$, $u = 0$;

ii) at $y = 0$, $\frac{\partial u}{\partial y} = \frac{1}{\mu_L}\frac{\partial \gamma}{\partial x} = \frac{1}{\mu_L}\frac{\Delta\gamma}{x_o}$;

iii) as $y \to (-\infty)$, $u \to 0$.

Using the substitution

$$t = \int_{o}^{x} \frac{dx}{u_i} \tag{7.8}$$

Equation 7.7 reduces to

$$\frac{\partial u}{\partial t} = \nu_L \frac{\partial^2 u}{\partial y^2} \tag{7.9}$$

The new boundary conditions are:

i) at $t = 0$, $u = 0$;

ii) at $y = 0$, $\frac{\partial u}{\partial y} = \frac{1}{\mu_L} \left(\frac{\Delta\gamma}{x_o}\right)$;

iii) as $y \to (-\infty)$, $u \to 0$.

It should be noted that t represents the time taken by a fluid element at the surface to travel a distance x along the surface of the cell. The solution to Equation 7.8 is given by [B2]

$$u = \frac{1}{\mu_L}\left(\frac{\Delta\gamma}{x_o}\right) y + \frac{1}{\mu_L}\left(\frac{\Delta\gamma}{x_o}\right) y \, \mathrm{erf}\left(\frac{y}{\sqrt{4\nu_L t}}\right) + \frac{2}{\mu_L}\left(\frac{\Delta\gamma}{x_o}\right)\left(\frac{\nu_L t}{\pi}\right)^{\frac{1}{2}} \exp\left(\frac{-y^2}{4\nu_L t}\right) \tag{7.10}$$

Therefore, the velocity at the surface is given by:

$$u_i = \frac{2}{\mu_L}\left(\frac{\Delta\gamma}{x_o}\right)\left(\frac{\nu_L t}{\pi}\right)^{\frac{1}{2}} \tag{7.11}$$

If one now defines an average velocity over the surface of the cell by the expression

$$u_i, \text{ avg} = \langle u_i \rangle = \frac{x_o}{t'} \quad \left(\text{where } t' = \int_{o}^{x_o} \frac{dx}{u_i}\right) \tag{7.12}$$

then substituting Equation 7.11 into 7.1 it can be shown that:

$$k_L = 2.12 \sqrt{\frac{D_L \langle u_i \rangle}{\pi \, x_o}} \tag{7.13}$$

$$\text{where,} \quad \langle u_i \rangle = \left[\frac{\Delta\gamma}{1.33\sqrt{\rho_L \mu_L x_o}} \right]^{\frac{2}{3}} \tag{7.14}$$

As in Case I if the values of $\Delta\gamma$ and x_o can be estimated, Equation 7.13 can be used to predict the corresponding value of k_L. As discussed subsequently, it is possible to obtain rough estimates of $\Delta\gamma$, for given values of x_o, under certain circumstances.

The equations derived above are for the case of an initially quiescent horizontal layer of liquid. The equations can, however, be used to obtain preliminary estimates in the case of flowing liquid phases in uniform rectilinear motion, i.e. in quasi-quiescent systems. In the latter case, the hydrodynamic situation in the presence of Marangoni instability is modelled by the superposition of cellular convective motion, of the type discussed above, on the initial undisturbed flow, the mean velocity of the convection cells in the direction of flow being assumed to be equal to the velocity of the liquid phase.

If the velocity at the surface of the cells is assumed to be constant over the cell (say, equal to the average value), and if t' and θ represent the time required for the elements at the surface of the convection cell to traverse the width x_o of the cell and the contact-time of the fluid elements in the absence of Marangoni convection, respectively, it can be deduced [L4] that the liquid-phase enhancement, E_L, assuming a constant value for the driving force for mass transfer, is given by:

$$E_L = \left(1 + \frac{R}{3}\right), \text{ if } R \leqslant 1 \tag{7.15a}$$

$$E_L = \left(\sqrt{R} + \frac{1}{3\sqrt{R}}\right), \text{ if } R > 1 \tag{7.15b}$$

$$\text{where,} \quad R = \frac{\theta}{t'}$$

In deriving the above expressions it was implicitly assumed that the instability manifests itself virtually instantaneously subsequent to the exposure of the liquid to the gas phase. It should be noted that as $\theta \to \infty$, $E_L \to \sqrt{R}$ as expected.

A 2-dimensional cell can be considered to be a section through a 3-dimensional cylindrical cell. The equations for a 3-dimensional cell would of course have to be modified to account for the radial "stretching" flow [S7] of the liquid from the centre towards the periphery of the cell. Moreover, a 3-dimensional cylindrical cell can be regarded as an approximate model for the polygonal convection cells observed experimentally [S1].

In this thesis we shall be concerned only with the 2-dimensional model analysed above. For the purposes of a priori prediction of k_L in the presence of Marangoni instability, one essentially requires information regarding the scale and the intensity of the established convective motion. An estimate of the cell size can be obtained using linear stability analysis. Implicit in the use of linear stability theory is the assumption that, whatever other effects non-linearity may have on the disturbance flow as it grows, the wave-length of the dominant (fastest-growing) disturbance remains practically unchanged. However, the estimates using linear stability theory have been shown to be in poor agreement with experimentally observed cell sizes for liquid-liquid systems [S1]. Non-linear theory has not as yet been developed to the stage where meaningful information regarding the cell size and/or the intensity of the convection can be deduced.

From a review of the literature it appears that the cell size is in general a function of the magnitude of the mass-transfer driving force, the physical properties of the liquid phase, and the liquid depth. An increase in the concentration driving force generally results in a

decrease in the average cell size. An increase in the depth of the liquid phase results in an increase in the cell size upto a critical liquid depth beyond which the depth of the liquid has essentially no effect on the cell size. It should be noted that in practice a distribution of cell sizes is generally observed.

It appears that at present it is not possible to obtain a priori estimates of the cell size and the intensity of the Marangoni convection. However, using the theory developed above one can obtain an estimate of the value of k_L for a given value of the cell size, x_o, provided that an estimate of $(\Delta\gamma)$ can be obtained.

In the case of Marangoni instability induced by the desorption of solutes for which the major resistance to transfer lies in the gas phase and where the hydrodynamics in the gas phase can be represented by the gas-side mass-transfer coefficient, a rough estimate of $\Delta\gamma$ can be obtained if the values of H, k_G, $(\frac{d\gamma}{dC})$, and D_L are known, and if, in addition, it is assumed that the difference in the concentration of the solute at the surface at the extremities of the cell is given by the penetration-theory expression for desorption of a solute from a quiescent liquid phase [see B14, Equation 48], using for the contact-time the time t' required by the elements of fluid at the surface of the cell to traverse the width x_o of the cell. The shear stress at the surface (assumed to be uniform) is obtained by dividing the difference in the values of the surface tension at the extremities of the cell by the width x_o of the cell.

The procedure for calculating the value of k_L for a given cell size, x_o, is given below.

1. Assume a value for the average velocity, $\langle u_i \rangle$, at the surface.

2. Calculate the effective exposure-time, $t' (= \frac{x_o}{\langle u_i \rangle})$, for the elements of liquid.

3. Calculate the value of $\Delta\gamma$ using the value of t' calculated above and Equation 48 in reference [B14].

4. Substitute the value of $\Delta\gamma$ in either Equation 7.2 or 7.14 as appropriate.

5. Check if the calculated value of $\langle u_i \rangle$ agrees with the value assumed in (1). If the values do not agree with each other, repeat the above procedure till agreement is obtained. It is most convenient to carry out this trial-and-error procedure graphically.

6. The value of k_L can be obtained by substituting the value of $\langle u_i \rangle$ calculated above into either Equation 7.5 or 7.13 as appropriate.

The above procedure can be repeated for different values of x_o, and a table of x_o versus the corresponding value of $\langle u_i \rangle$ can be constructed. Reference to a single experimentally obtained value of k_L (or E_L) would enable the evaluation of the values of x_o and $\langle u_i \rangle$, as predicted by the theory, for the conditions of the experiment. It should be remembered that x_o is in general a function of the liquid depth, the concentration driving force and the physical properties of the liquid.

For the sake of illustration, the theory developed above will be applied to the case of desorption of acetone from a 0.5 wt. % aqueous solution into air at atmospheric pressure. The bulk gas concentration of acetone will be assumed to be negligible, and the liquid will be assumed to be semi-infinite and initially quiescent. The values of the relevant parameters required for the calculation (see Appendix 1) are

given below.

1) $D_L = 1.27 \times 10^{-5}$ cm^2/s.

2) Concentration of acetone in the bulk liquid, $C_b = 0.086 \times 10^{-3}$ $\frac{\text{gmole}}{\text{cm}^3}$.

3) $\left|\frac{d\gamma}{dC}\right| = 32.33 \times 10^3 \frac{\text{dyn cm}^2}{\text{gmole}}$.

4) $k_G = 3 \times 10^{-5} \frac{\text{gmole}}{\text{cm}^2 \text{ s atm}}$.

5) Henry's Law constant, $H = 29.5 \frac{\text{cm}^3 \text{ atm}}{\text{gmole}}$.

Using the theory (Case II) developed above, estimates of $\langle u_i \rangle$ and $\Delta\gamma$ are obtained for various values of x_o and, together with the corresponding predicted values of k_L, are listed in Table 1.

Table 1

	x_o, cm		
	0.01	0.1	0.5
$\langle u_i \rangle$, cm/s	2.55	2.42	2.40
$\Delta\gamma$, dyn/cm	0.051	0.15	0.33
k_L, cm/s	6.8×10^{-2}	2.1×10^{-2}	9.4×10^{-3}
$t' = \frac{x_o}{\langle u_i \rangle}$, seconds	3.92×10^{-3}	41.32×10^{-3}	0.208
$\frac{\Delta\gamma \langle u_i \rangle}{x_o}$, ergs/cm^{2}s	12.9	3.63	1.58

The quantity $\left[\frac{\Delta\gamma\langle u_i\rangle}{x_o}\right]$ is a rough estimate of the rate of work done per unit area of surface by the forces acting at the surface of the liquid. At steady state, this should be equal to the rate of dissipation of energy by viscous forces in the bulk of the liquid associated with unit surface area. In making the above calculations, it was assumed that the concentration of solute in the elements of liquid reaching the surface (owing to the cellular convection) is equal to that in the bulk liquid. It should be noted that for sufficiently large values of the overall exposure-time, the elements of fluid reaching the surface may not be representative of the conditions in the bulk; e.g. in the case of deep pools of liquid, even though the concentration of solute at a sufficiently large depth may be virtually unchanged during the transfer process, the layer of liquid immediately beneath the surface may be substantially depleted of solute as a result of the cellular convective flows.

One very interesting result that emerges from the calculations is that the intracellular surface-tension difference does not have to be large (e.g. of the order of several dynes/cm) for the Marangoni effect to be of substantial significance.

For the sake of further illustration, assume that in the case of desorption of acetone under conditions similar to those discussed above, it has been experimentally determined that the resulting Marangoni instability enhances the liquid-side mass-transfer coefficient by a factor of 1.82 for an overall exposure-time of 0.2 seconds. Making use of Equation 7.15, the theory indicates that $\frac{x_o}{\langle u_i\rangle} = 0.08$ s. Interpolating the data shown in Table 1, the theory predicts that $x_o \cong 0.18$ cm, and $\langle u_i\rangle \cong 2.42$ cm/s. Because of the assumptions involved in the development of the theory, the estimates obtained should be regarded only as preliminary.

Finally, it must be stated that it is possible, for the model analysed above, to carry out a numerical analysis of the complete set of equations for motion and mass transfer [N1]. In this case, too, the value of x_o would have to be known in advance if the analysis were not to be considered as semi-theoretical. However, owing to the lack of a complete understanding of the phenomena at present and the necessity for making a large number of assumptions, not all of them necessarily justified, it is preferable to use simpler, even though inherently less accurate, theoretical methods such as the one developed above. In cases where an estimate of $\Delta\gamma$ cannot be obtained independently for a given value of x_o, a numerical solution appears to be the only route available. A detailed discussion of the numerical approach is, however, outside the scope of this thesis.

7B: SOME ASPECTS REGARDING THE MANIFESTATION OF THE MARANGONI EFFECT IN INDUSTRIAL CONTACTORS

A brief qualitative discussion of some of the salient aspects of surface-tension driven convection in typical gas-absorption equipment is given below. As mentioned earlier in this thesis (Chapter Two), previous theoretical analyses to determine the conditions for the occurrence of Marangoni instability in gas-liquid systems have dealt with non-flow systems, i.e. systems which are quiescent in the initial unperturbed state. It seems likely, however, that the results obtained are qualitatively valid for flow systems as well. Further study is needed to extend these analyses to systems where the gas and liquid phases are in relative motion in the unperturbed state, and to cases where the bulk gas and liquid phases are in turbulent flow.

An important result determined experimentally is that, under the

conditions normally encountered in practice, the Marangoni effect appears to have no influence on the value of the gas-phase mass-transfer coefficient, k_G. This result has obvious implications for systems wherein the major resistance to solute transfer lies in the gas phase. Moreover, it follows that the presence or absence of the Marangoni phenomenon in a given system cannot be inferred from measurements on the rate of mass transfer of a solute for which the resistance to transfer is essentially in the gas phase. The influence of Marangoni convection is therefore in general restricted to its effect on the value of the liquid-side mass-transfer coefficient, k_L, and the effective interfacial area of contact, $\underline{a}$. The influence of the Marangoni effect on the values of k_L and $\underline{a}$ is discussed below with respect to absorption in packed and plate columns.

In packed columns the liquid flows as a film over the surface of the packing, and is apparently periodically rejuvenated [D2] at the discontinuities existing at the packing junctions. Work reported in this thesis has shown that in general the value of the liquid-side mass-transfer coefficient can be substantially increased due to the occurrence of Marangoni convection. Under certain circumstances, e.g. during the absorption of solutes which lower the surface tension, the occurrence of a point-to-point variation in the surface tension, due in turn to a variation in the local thickness and/or velocity of the liquid film, may result in the break-up of the liquid film into rivulets and consequently to a substantial decrease in the effective interfacial area [B8,N3,W1]. The effect of the break-up of the film into rivulets on the value of k_L is uncertain; it is possible that the value of k_L in the resulting rivulet-flow regime may be slightly higher relative to the value for the original film flow. Moreover, in the case discussed above, the liquid

phase is susceptible to oscillatory Marangoni instability [L3,S9] and, in the case of turbulent gas flow, to additional interfacial disturbances caused by eddies of solute-rich gas from the bulk gas phase reaching the surface. Hence, the decrease in the value of the liquid-side volumetric mass-transfer coefficient, $k_L\underline{a}$, may not be proportional to the decrease in $\underline{a}$ because of the possibility of an increase in the value of k_L. In the case of the gas-side volumetric mass-transfer coefficient, $k_G\underline{a}$, the decrease will be due solely to the decrease in the value of $\underline{a}$, the value of k_G being virtually independent of the hydrodynamic conditions in the liquid phase and the degree of wetting of the packing surface.

In the case of plate columns, too, there exists some evidence [V4] that the occurrence of the Marangoni effect may result in an appreciable increase in the value of k_L. It should be noted that the liquid phase in such contactors is characterised by a high degree of turbulence in the bulk. The manifestation of surface-tension driven convection in turbulent systems is a complex phenomenon influenced by many diverse factors. In sieve-plate columns, surface-tension induced convection may result in a dramatic change in the value of $\underline{a}$ by accelerating or retarding the coalescence of individual bubbles in the froth (or foam) on the plate [B5]. This effect is likely to be much less dramatic in the case of bubble-cap plates.

Finally, in view of the many factors which influence the occurrence and intensity of the Marangoni effect, it is uncertain to what extent it can be quantitatively accounted for in the design of industrial gas-absorption equipment. However, an important need of at least a semi-quantitative understanding of the phenomenon lies in determining whether anomalous experimental data obtained in laboratory apparatus, which may

be used as a basis for the design of an industrial plant, have been obtained under conditions of instability which may not be representative of plant conditions.

CHAPTER EIGHT

SUGGESTIONS FOR FUTURE WORK

In the light of the work reported in this thesis and a critical review of the literature, some recommendations and suggestions for further investigations on the Marangoni phenomenon are given below.

1. Previous theoretical analyses have in general studied the occurrence of Marangoni instability in gas-liquid systems during the physical transport of a solute between the phases, assuming the fluid phases to be quiescent in the initial unperturbed state. It would be useful to extend the work to flow systems, and also to cases where the transfer of the solute is accompanied by simultaneous chemical reaction in the liquid phase.

2. Previous optical studies have in general been concerned only with the qualitative description of the morphology of the convective flows induced by the Marangoni instability. It would be interesting to obtain information about the intensity of the convective motion, and to examine the effect of various factors such as the physical properties of the liquid, the overall concentration driving force, and the liquid depth on the scale of the resulting convective flows. In addition, it would be useful to develop a technique to investigate the morphology of the Marangoni convection in flow systems such as wetted-wall columns and laminar jet apparatus.

3. It would be worthwhile, from a practical point of view, to extend the investigations in the packed column to cover a wider range of operating parameters and a variety of systems. Specifically, it would be interesting to study the effect of the viscosity of the

liquid phase and the presence of minute amounts of deliberately introduced surface-active agents on the enhancement in the liquid phase. It would also be of some practical importance to investigate the effect of Marangoni convection, if any, in other types of contactors used industrially, e.g. plate columns, bubble columns, mechanically agitated contactors etc. In this connection, the interaction between "natural" turbulence and the Marangoni effect is worth elucidating.

4. Further work, possibly with a variety of different solutes, is required to elucidate unambiguously the effect of k_G on the enhancement in the liquid phase in order to make an objective appraisal of the speculations outlined in Chapter 3. In this connection, it would be useful to develop an apparatus in which the value of k_G can be varied by at least an order of magnitude without significantly affecting the value of k_L^*.

5. It would be instructive from a fundamental point of view to make detailed investigations on the effect of the hydrodynamic nature of the unperturbed liquid flow on the growth and morphology of convective motion induced by Marangoni instability.

6. The possibility of obtaining meaningful information about the rate of growth of Marangoni instability by means of a numerical analysis of the complete set of the transient equations for mass and momentum transfer, based on a relatively simple model of Marangoni convection, should be investigated.

7. The reasons for the apparent absence of Marangoni convection during the absorption of CO_2 into aqueous monoethanolamine (MEA) solutions in the packed column should be thoroughly investigated. In this connection, additional information about the occurrence or otherwise of the Marangoni

effect during the absorption of CO_2 into aqueous solutions of MEA under different hydrodynamic conditions would be useful, and experiments should therefore be carried out to investigate the occurrence of the Marangoni effect in the modified stirred-cell apparatus, using an inert tracer to monitor the values of k_L.

8. The simple preliminary semi-theoretical analysis, based on a two-dimensional model of cellular convection, developed in Chapter 7 should be refined and extended. In particular, it would be useful to develop a method for predicting the cell size under conditions of cellular Marangoni instability. Experiments to test the theory should be devised, wherein information on the size of the cells formed can be obtained together with measurements on the rate of gas absorption.

9. Any anomalous results obtained in the course of laboratory studies on gas absorption should be scrutinized for the occurrence of the Marangoni effect. In the case of experiments carried out with the objective of obtaining data to be used subsequently in the design of an industrial plant, it would be a wise practice to check for the occurrence of Marangoni convection using the tracer-desorption technique. If in a plant a transfer process is aided by previously unsuspected, and hence unaccounted for, Marangoni convection, one has an overdesigned plant. On the other hand if a design is based on data obtained under instability conditions not available in the plant, one has a full-scale "disaster".

APPENDIX ONE

RELEVANT PHYSICO-CHEMICAL PROPERTIES OF THE CHEMICALS USED AND ANALYTICAL METHODS

The relevant physico-chemical properties of the solutes employed at 25°C and, where relevant, at 1 atmosphere pressure are given below together with the analytical techniques used for the determination of carbon dioxide and acetone in dilute aqueous solutions.

A1.1 Acetone

i) $D_L = 1.27 \times 10^{-5}$ cm^2/s (source: M2).

ii) $D_G = 0.104$ cm^2/s (source: M2).

iii) Henry's-law constant, $H = 29.5 \frac{\text{cm}^3 \text{ atm}}{\text{gmole}}$ (source: M2).

iv) Density of the aqueous solutions (g/cm^3),

$$\rho_L = \rho_w - 0.117 \times 10^{-2}x - 0.904 \times 10^{-5}x^2 - 0.56 \times 10^{-8}x^3$$

where, x = concentration of acetone, wt. %,

and ρ_w = density of water, g/cm^3.

The equation is valid for values of x between 0 and 100 (source: P2).

v) The relative surface tensions of dilute aqueous solutions of acetone are shown in Figure A1-1.

A1.2 Ethyl Ether

i) $D_L = 0.962 \times 10^{-5}$ cm^2/s (source: M2).

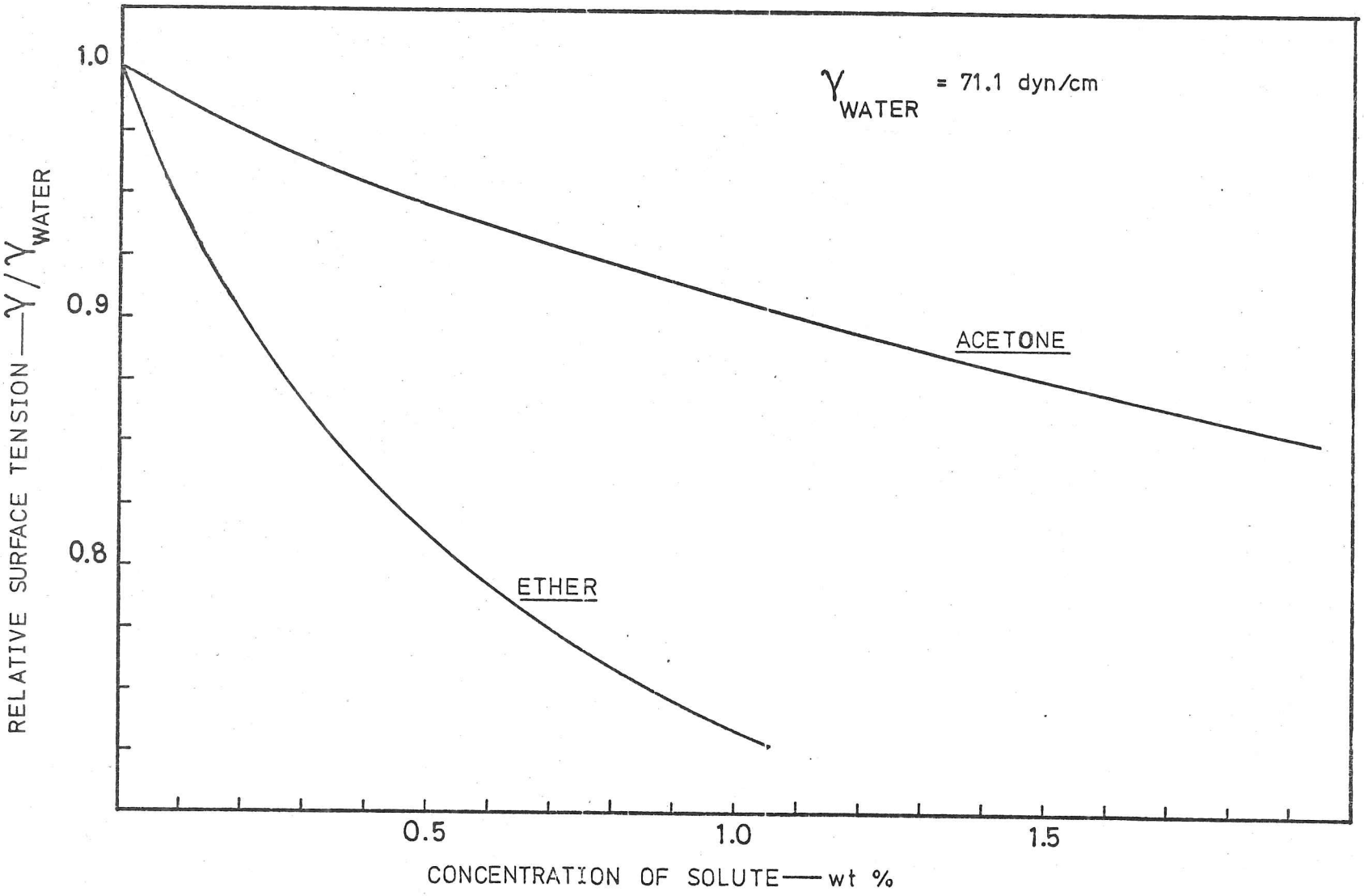

FIG. A1-1 RELATIVE SURFACE TENSIONS OF DILUTE AQUEOUS SOLUTIONS AT 25° C (AFTER MAYR[M2])

ii) $D_G = 0.088\ cm^2/s$ (source: M2).

iii) $H = 897.4\ atm\ cm^3/gmole$ (source: M2).

iv) Density of dilute aqueous solutions (g/cm^3),

$$\rho_L = \rho_w - 0.221 \times 10^{-2}x + 0.35 \times 10^{-4}x^2$$

where, x = concentration of ether, wt. %,

and ρ_w = density of water, g/cm^3.

The equation is valid for values of x between 0 and 4.5 (source: P2).

v) The relative surface tensions of dilute aqueous solutions of ether are shown in Figure A1-1.

A1.3 Carbon Dioxide

i) $D_L = 1.92 \times 10^{-5}\ cm^2/s$ (source: S6).

ii) $H = 29762\ \frac{cm^3\ atm}{gmole}$ (source: S6).

iii) The value of the second order rate-constant for the reaction between CO_2 and MEA is equal to 7600 l/gmole s (source: S6).

A1.4 The Determination of CO_2 in Water

The concentration of dissolved carbon dioxide in water was determined by a standard volumetric method [T5]. A known amount of the sample to be analysed was added to a solution containing a known amount of NaOH kept in a standard volumetric flask. The amount of NaOH in the solution was in excess of that required for the complete conversion of CO_2 in the sample to carbonate.

$$CO_2 + 2OH^- \rightarrow CO_3^{--} + H_2O$$

An excess of $BaCl_2$ was then added to precipitate the carbonate in solution as virtually insoluble barium carbonate. The excess NaOH was back-titrated against standard HCl using phenolphthalein as the indicator, and the amount of CO_2 in the sample was calculated from the amount of NaOH consumed. During sampling, care was taken to prevent any desorption of CO_2 from the sample; this was achieved by immersing the exit of the sampling-tube, while taking a sample, beneath the surface of the NaOH solution in the volumetric flask.

A1.5 The Determination of Acetone in Dilute Aqueous Solutions

The concentration of acetone in dilute aqueous solutions was determined by means of a standard volumetric method. The method depends on the formation of iodoform by the action of iodine on acetone under controlled alkaline conditions. The volume of standard iodine solution that reacts with the acetone in the sample is a measure of the amount of acetone in the sample. Details of the procedure are available in the literature [S10].

$$1 \text{ ml of N/10 } I_2 \equiv 0.968 \times 10^{-3} \text{g of acetone.}$$

APPENDIX TWO

DIMENSIONAL ANALYSIS OF MARANGONI INSTABILITY INDUCED BY THE DESORPTION OF SOLUTES WHICH LOWER THE SURFACE TENSION

In this section the technique of dimensional analysis is used to obtain a set of dimensionless groups or ratios from a list of the pertinent variables (physical quantities) involved in the case of gas-liquid systems subject to Marangoni convection induced by the desorption of solutes which lower the surface tension. These dimensionless groups may be used as a basis for the description of such systems.

In order to carry out the analysis, the following quantities are chosen arbitrarily as the "primary" quantities: 1) mass - M; 2) length - L; 3) time - T; 4) moles (of solute) - M_o; and 5) temperature - θ. The units of measurement are taken to be gram, cm, second, g mole, and degree Kelvin respectively.

The variables which are considered to be relevant are listed below together with their corresponding dimension(s).

Variable	Dimension(s)
1) k_L - liquid-phase mass-transfer coefficient in the presence of Marangoni instability	L^1T^{-1}
2) k_L^* - liquid-phase mass-transfer coefficient in the unperturbed state	L^1T^{-1}
3) H - Henry's-law constant	$M^1M_o^{-1}L^2T^{-2}$
4) k_G - gas-phase mass-transfer coefficient	$M^{-1}M_o^1L^{-1}T^1$

Variable	Dimension(s)
5) (ΔC_L) - average concentration driving force in the liquid phase	$M_o^1 L^{-3}$
6) $(-\frac{\partial \gamma}{\partial C})$ - negative of the rate of variation of surface tension with respect to the solute concentration in the liquid phase	$M^1 M_o^{-1} L^3 T^{-2}$
7) μ_L - viscosity of the liquid	$M^1 L^{-1} T^{-1}$
8) ρ_L - density of the liquid	$M^1 L^{-3}$
9) D_L - solute diffusivity in the liquid	$L^2 T^{-1}$
10) θ - temperature of the liquid phase	$\underline{\theta}^1$
11) R_g - the gas constant	$M^1 M_o^{-1} L^2 T^{-2} \underline{\theta}^{-1}$
12) d - depth of the liquid phase	L^1

The temperature in the liquid phase is assumed to be uniform. The quantity k_L may be considered to be the dependent variable. Using the method devised by Taylor [T1], the following set of dimensionless ratios is obtained:

1) $\frac{k_L}{k_L^*} = E_L$, the liquid-phase enhancement factor;

2) $\frac{Hk_G}{k_L^*} = R_r$, the ratio of resistances;

3) $(-\frac{\partial \gamma}{\partial C}) \frac{(\Delta C_L)}{\mu_L k_L^*} = N_{Ma}$, the Marangoni number;

4) $(\frac{R_g \theta}{H})$;

5) $\left(\frac{\mu_L}{\rho_L D_L}\right) = N_{Sc}$, the Schmidt number;

6) $\frac{1}{R_g \theta}\left(-\frac{\partial \gamma}{\partial C}\right)\frac{k_L^*}{D_L}$;

7) $\frac{k_L^* d}{D_L}$, a type of Sherwood number.

If the depth of the liquid can be regarded as infinite for all practical purposes, the dimensionless ratio $(k_L^* d/D_L)$ is in such cases redundant. In addition, if the solute is only weakly adsorbed at the interface, the dimensionless ratio $\frac{1}{R_g \theta}\left(-\frac{\partial \gamma}{\partial C}\right)\frac{k_L^*}{D_L}$ may be unimportant.

APPENDIX THREE

THE ABSORPTION OF SOLUTES WHICH LOWER THE SURFACE TENSION IN A PACKED COLUMN

A3.1 Introduction

The absorption of solutes which depress the surface tension is a fairly common industrial process. The mechanism of absorption in such cases may be complicated by interfacial effects, hitherto largely ignored, which are discussed below. The theoretical analysis of Sternling and Scriven [S9] showed that the transfer of a solute which lowers the surface tension from the gas phase into the liquid phase is susceptible to oscillatory Marangoni instability. This theoretical prediction has been verified in the case of non-flow systems by Linde et al. [L3] for aqueous as well as non-aqueous systems. In addition, Ellis and Biddulph [E1] observed to-and-fro convective motion at the surface of a horizontal laminar film of water during the absorption of acetone and methanol from the gas phase (air). Furthermore, in the case of a liquid flowing as a thin film over a solid supporting surface, absorption of solutes which depress the surface tension may result in the break-up of the film into rivulets, resulting thereby in a severe reduction in the interfacial area of contact [B8,N3,W1]. It was decided, therefore, to carry out some preliminary experiments in order to assess the effect, if any, of the above phenomena on the value of $k_L a$ during the absorption of acetone into water in a packed column. Acetone was absorbed from acetone-CO_2 gas mixtures into water. The rate of absorption of CO_2 was measured and used to calculate the values of $k_L a$.

A3.2 Apparatus and Procedure

The packed column was the same as that used previously. The packing used was 0.95 cm Raschig rings, and the packed volume was 115 cm^3. The auxiliary apparatus was similar to that described previously. The entire assembly was kept in a constant-temperature room maintained at approximately 25°C, and the pressure within the system was virtually atmospheric. The partial pressure of acetone in the inlet gas stream was varied by passing a part of the CO_2 stream through a series of bubblers containing pure acetone and kept in a water-bath maintained at approximately 25°C. The liquid phase was once-distilled water. The concentration of dissolved CO_2 in the inlet liquid (nearly zero) and that in the outlet liquid was determined titrimetrically. The liquid was assumed to be in plug flow.

In order to calculate the concentration of dissolved CO_2 at the surface of the liquid, the partial pressure of CO_2 in the gas phase at the interface must be known. It is interesting to note that in the case considered above, the partial pressure of CO_2 in the bulk gas phase in general differs appreciably from that at the interface although the transfer of CO_2 is "liquid-film controlled". This is because the transfer of acetone is essentially gas-film controlled, and hence the partial pressure of acetone at the interface is a very small percentage of that in the bulk gas. If the total pressure in the gas phase is uniform, the partial pressure of CO_2 must increase correspondingly such that the sum of the two partial pressures is equal to the total pressure (the small contribution due to vapour pressure of water being neglected) at all points in the gas film. In order to obtain an approximate estimate of the partial pressure of CO_2 at the interface the following procedure was adopted.

The partial pressure of acetone at the interface was calculated on

the basis of the two-film theory, using for the partial pressure of acetone in the bulk gas the estimated average value of the partial pressure of acetone in the column, and assuming for the purposes of calculation that the CO_2 in the gas phase behaves as an inert. The relevant values of $k_G\underline{a}$ were obtained by extrapolating the data reported by Vidwans and Sharma [V3], as suggested by those authors. The $k_G\underline{a}$ data were corrected for the effect of solute diffusivity ($k_G \propto D_G^{0.5}$) and for the effect of the concentration level of the solute in the gas phase [V5]. In correcting for the latter effect, the value of the correction factor was based on the conditions existing at the bottom of the column. The calculations showed that the partial pressure of acetone at the interface was approximately 5 per cent of that in the bulk and therefore, in the range investigated, it would be reasonable to assume, at least as a first approximation, that the partial pressure of CO_2 at the gas-liquid interface was practically equal to the total pressure.

The values of $k_L\underline{a}$ were calculated by means of the equation

$$\ln \left[\frac{C_i - C_{b,T}}{C_i - C_{b,B}} \right] = \frac{k_L\underline{a}\, V}{L} \qquad \text{(A3.1)}$$

where, C_i ≡ concentration of dissolved CO_2 at the interface, gmole/cm^3;

$C_{b,T}$ ≡ concentration of dissolved CO_2 in the bulk liquid at the inlet, gmole/cm^3;

$C_{b,B}$ ≡ concentration of dissolved CO_2 in the bulk liquid at the outlet, gmole/cm^3;

V ≡ packed volume, cm^3;

L ≡ liquid flow rate, cm^3/s.

The acetone in the outlet gas was scrubbed in a second absorber before the gas was vented to the atmosphere. For reasons of economy, only low gas flow rates were used in this study. The gas-phase superficial velocity was varied from around 2.3 cm/s to 5.75 cm/s. The liquid-phase superficial velocity was varied from 0.18 cm/s to 0.38 cm/s. The partial pressure of acetone in the inlet gas was varied from zero to about 206 mm Hg.

A3.3 Results and Discussion

For the range of variables investigated, the values of $k_L a$ obtained were found to be virtually independent of the partial pressure of acetone in the gas phase and the gas flow rate, and were in good agreement with the values of $(k_L a)^*$ reported in Chapter 3. In other words, the absorption of acetone did not appear to have a significant effect on the hydrodynamics of the flowing liquid film. The rise in temperature of the bulk liquid as a result of the absorption process was small enough to be neglected. The above result, however, may not be conclusive because of the approximate nature of the investigation and the restricted range of variables studied. A more refined and detailed study should be carried out. It would be of interest to measure the values of $k_G a$ and $k_L a$ simultaneously. A decrease in the observed value of $k_G a$, for a fixed gas flow rate and correcting for the effect of solute concentration-level, would be due essentially to a decrease in the value of a.

APPENDIX FOUR

MARANGONI INSTABILITY DURING GAS ABSORPTION WITH SIMULTANEOUS CHEMICAL REACTION

A4.1 Introduction

There is practically no information available in the literature regarding the theoretical prediction of the conditions for the occurrence of Marangoni instability in gas-liquid systems wherein the dissolved gas undergoes a chemical reaction in the liquid phase. In particular, the case where the products of the reaction lead to an increase in the surface tension has not been studied. It appears likely that such a situation prevails during the absorption of CO_2 into aqueous solutions of monoethanolamine [D2]; the products of the reaction between CO_2 and monoethanolamine are ions. It was therefore decided to make a preliminary analysis of such systems using linear stability theory.

A4.2 Description of the Unperturbed System

The system to be analysed is shown schematically in Figure A4-1. The liquid phase is assumed to be semi-infinite and initially quiescent. The gas phase consists of pure A which dissolves in the liquid and undergoes a first-order irreversible reaction in the liquid phase given by

$$A \rightarrow C \qquad \text{(A4.1)}$$

The product C is assumed to be non-volatile, and is such that an increase in the concentration of C in the liquid results in an increase in the surface tension.

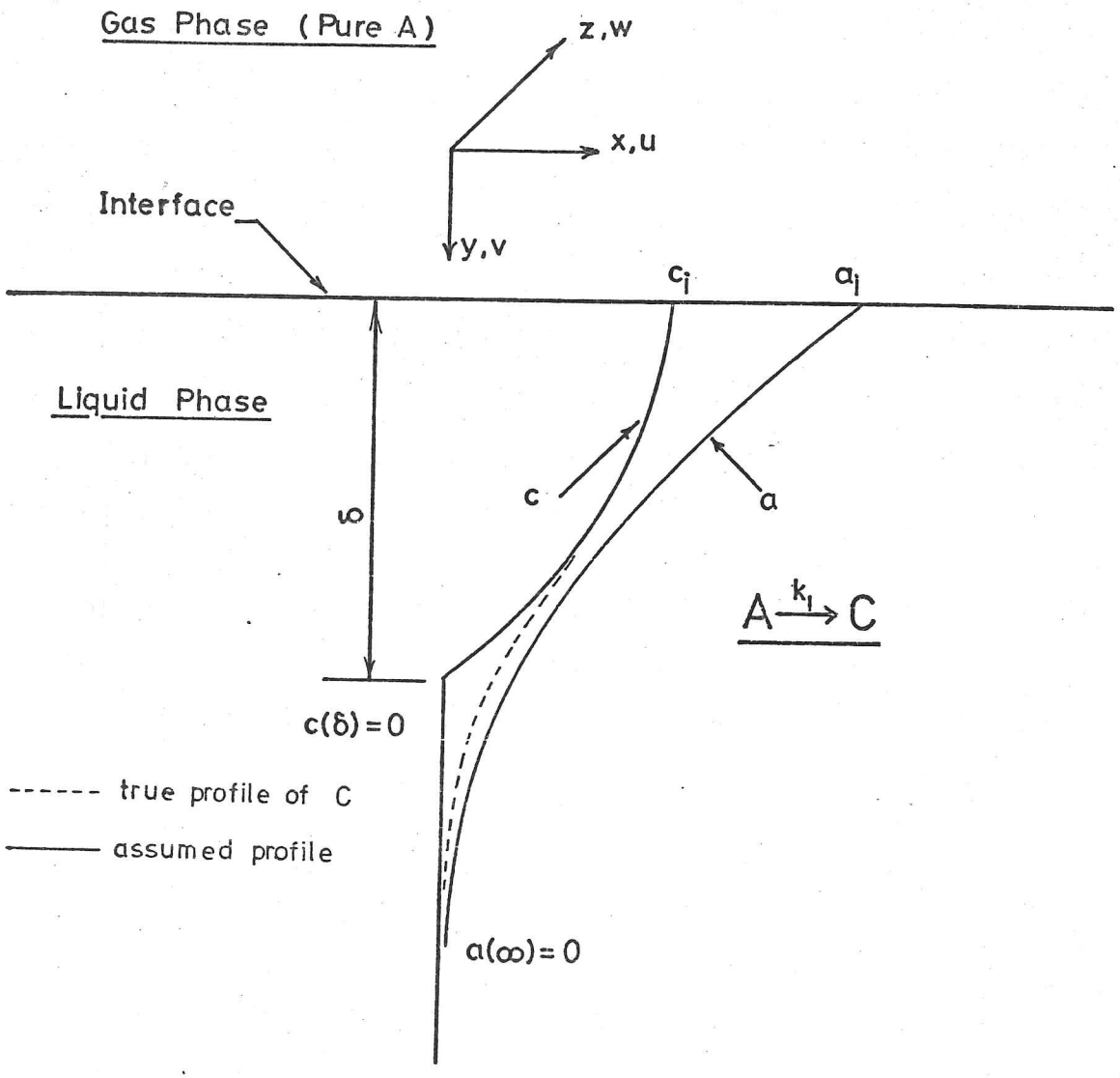

FIG. A4-1 SCHEMATIC DIAGRAM OF THE CONCENTRATION PROFILES IN THE INITIAL UNPERTURBED STATE

Consider that at time t = 0 the liquid is exposed to the gas phase containing pure A. At any subsequent time t (t > 0) there will exist concentration profiles of A and C within the liquid phase which in general will vary with time. The 'frozen-profile' technique [B14] is used to investigate the stability of the system. This technique is essentially an artifice wherein the stability of the system at any given instant in time is investigated by 'freezing' the concentration profiles existing at that time and assuming the resultant 'frozen' state to be the pseudo-stationary initial unperturbed state. The assumption implicit in the above technique is that the instability manifests itself in a time small enough for the concentration profiles to remain virtually unchanged.

For the purposes of this preliminary investigation, the concentration profile of the product C is approximated as shown in the figure. The concentration of C is assumed to fall to zero at a depth δ within the liquid phase. The value of δ is in general a function of time. In addition, the following assumptions are made:

1) the diffusivities of all the species in the liquid are assumed to be equal;

2) the gas-liquid interface is planar and inflexible;

3) temperature effects are negligible;

4) the surface tension is a function only of the concentration of the product C at the interface;

5) the liquid phase is non-volatile;

6) oscillatory instability (overstability) is assumed to be absent in the state of neutral stability, and surface viscosity and elasticity effects are assumed to be negligible.

Moreover, the analysis is restricted to relatively large values of $k_1 t$ ($k_1 t \gg 1$), where k_1 is the first-order reaction rate-constant and t is the exposure-time of the elements of the liquid in the initial state. The co-ordinate axes are such that the x-z plane lies in the plane of the interface, and the positive direction of the y axis is in the direction of increasing liquid depth. For values of $k_1 t \gg 1$, the concentration of A is given by [D2]

$$\frac{a}{a_i} = \exp\left(- y\sqrt{\frac{k_1}{D_L}}\right) \qquad \text{(A4.2)}$$

where, a = concentration of A in the liquid;

a_i = concentration of A at the interface;

D_L = diffusivity of A in the liquid.

The concentration gradient of C is assumed to be given by

$$\frac{\partial c}{\partial y} = a_i\sqrt{\frac{k_1}{D_L}}\left[\exp\left(- y\sqrt{\frac{k_1}{D_L}}\right) - 1\right]$$

$$\text{for } 0 < y \leqslant \delta \qquad \text{(A4.3a)}$$

$$\text{and } \frac{\partial c}{\partial y} = 0 \text{ for } y > \delta \qquad \text{(A4.3b)}$$

where c is the concentration of C in the liquid. An expression for estimating the value of δ is given later in this analysis. In the initial unperturbed state a and c are independent of x and z.

A4.3 Formal Description of the Perturbed State

Let $\hat{a}$, $\hat{c}$, $\hat{u}$, $\hat{v}$, and $\hat{w}$ represent the concentrations of A and C and the velocity components in the x, y, and z directions, respectively, in the liquid in the initial pseudo-steady state ($\hat{u} = \hat{v} = \hat{w} = 0$).

Furthermore, let a', c', u', v', and w' be the infinitesimal perturbations in the disturbed state such that the perturbed variables are given by $a = \hat{a} + a'$, $c = \hat{c} + c'$ .... etc. Then the linearised equations for motion and mass transfer are given by

$$(\frac{\partial}{\partial\theta} - \nu_L\nabla^2)\nabla^2 v' = 0 \qquad \text{(A4.4a)}$$

$$(\frac{\partial}{\partial\theta} - D_L\nabla^2)a' + k_1 a' = - v' \frac{\partial\hat{a}}{\partial y} \qquad \text{(A4.4b)}$$

$$(\frac{\partial}{\partial\theta} - D_L\nabla^2)c' - k_1 a' = - v' \frac{\partial\hat{c}}{\partial y} \qquad \text{(A4.4c)}$$

where, θ = time subsequent to the introduction of the perturbations;

∇^2 = Laplacian operator;

ν_L = kinematic viscosity of the liquid phase.

The boundary conditions are:

i) at $y = 0$

$$v' = 0;\ \mu_L \frac{\partial^2 v'}{\partial y^2} = \sigma\nabla_1{}^2 c';\ a' = 0;\ \frac{\partial c'}{\partial y} = 0;$$

where, $\nabla_1{}^2 \equiv (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2})$ and $\sigma = (\frac{d\gamma}{dc})_{c=\hat{c}_i}$.

ii) for $y \to \infty$,

$$v' = \frac{\partial v'}{\partial y} = a' = c' = 0.$$

Introducing the dimensionless variables

$$(\bar{a}', \bar{c}', \bar{v}', \bar{\theta}) \equiv (\frac{a'}{\hat{a}_i}, \frac{c'}{\hat{a}_i}, \frac{v'}{\sqrt{D_L k_1}}, k_1\theta)$$

and

$$(\xi, \eta, \zeta) \equiv (x\sqrt{\frac{k_1}{D_L}}, y\sqrt{\frac{k_1}{D_L}}, z\sqrt{\frac{k_1}{D_L}})$$

the Equations A4.4 are transformed into their dimensionless form given by

$$\left(\frac{\partial}{\partial\bar{\theta}} - (N_{Sc})\bar{\nabla}^2\right)\bar{\nabla}^2\bar{v}' = 0 \qquad \text{(A4.5a)}$$

$$\left(\frac{\partial}{\partial\bar{\theta}} - \bar{\nabla}^2\right)\bar{a}' = -\bar{v}'\frac{\partial\bar{\hat{a}}}{\partial\eta} - \bar{a}' \qquad \text{(A4.5b)}$$

$$\left(\frac{\partial}{\partial\bar{\theta}} - \bar{\nabla}^2\right)\bar{c}' = -\bar{v}'\frac{\partial\bar{\hat{c}}}{\partial\eta} + \bar{a}' \qquad \text{(A4.5c)}$$

The boundary conditions in the dimensionless form are given by:

i) at $\eta = 0$,

$\bar{v}' = 0$; $\frac{\partial^2\bar{v}'}{\partial\eta^2} = (N_{Ma})\bar{\nabla}_1{}^2\bar{c}'$;

$\bar{a}' = 0$; $\frac{\partial\bar{c}'}{\partial\eta} = 0$; where,

N_{Ma} = Marangoni number = $\left(\frac{\sigma\hat{a}_i}{\mu_L\sqrt{D_L k_1}}\right)$, and

N_{Sc} = Schmidt number = $\left(\frac{\mu_L}{\rho_L D_L}\right)$.

ii) for $\eta \to \infty$,

$$\bar{v}' = \frac{\partial\bar{v}'}{\partial\eta} = \bar{a}' = \bar{c}' = 0.$$

The perturbations are assumed to be of the form given by

$$\bar{v}' = F(\xi,\zeta)f(\eta)e^{(p\bar{\theta})} \qquad \text{(A4.6a)}$$

$$\bar{a}' = F(\xi,\zeta)g(\eta)e^{(p\bar{\theta})} \qquad \text{(A4.6b)}$$

$$\bar{c}' = F(\xi,\zeta)h(\eta)e^{(p\bar{\theta})} \qquad \text{(A4.6c)}$$

The function $F(\xi,\zeta)$ describes a periodic variation in the x-z plane, and is defined by

$$\bar{\nabla}_1{}^2F = \frac{\partial^2F}{\partial\xi^2} + \frac{\partial^2F}{\partial\zeta^2} = -\alpha^2F \qquad \text{(A4.6d)}$$

where α is the dimensionless wave number for the periodic variation. Equations A4.2 and A4.3 in dimensionless variables are given by, respectively,

$$\bar{\hat{a}} = e^{-\eta} \tag{A4.7}$$

and

$$\frac{\partial \bar{\hat{c}}}{\partial \eta} = e^{-\eta} - 1 \quad \text{for} \quad 0 < \eta \leq \bar{\delta} \tag{A4.8A}$$

$$= 0 \quad \text{for} \quad \eta > \bar{\delta} \tag{A4.8b}$$

Substituting Equations A4.6 into A4.5 yields the differential equations defining f, g, and h:

$$[p - (N_{Sc})(D^2-\alpha^2)](D^2-\alpha^2)f = 0 \tag{A4.9a}$$

$$[p - (D^2-\alpha^2)]g + g = - f \frac{d\bar{\hat{a}}}{d\eta} \tag{A4.9b}$$

$$[p - (D^2-\alpha^2)]h - g = - f \frac{d\bar{\hat{c}}}{d\eta} \tag{A4.9c}$$

where, $D^2 \equiv \frac{d^2}{d\eta^2}$

In seeking solutions for the case of neutral stability, the value of p will be taken to be equal to zero. The boundary conditions are given by:

$$f(o) = g(o) = h'(o) = 0 \; ; \; f''(o) = -\alpha^2(N_{Ma})h(o) \; ;$$

$$\text{and} \quad f(\infty) = f'(\infty) = g(\infty) = h(\infty) = 0 \; ;$$

where the prime denotes differentiation with respect to η.

In common with other workers [B14,S9], the solution of the Equations A4.9, subject to the boundary conditions given above and p equals zero, is obtained as a relation between the Marangoni number and the dimensionless wave number, i.e. the curve of neutral stability. The detailed algebraic manipulations are not given here, and only the final result is stated below.

$$N_{Ma} = \frac{8\alpha^2}{2(\alpha+1)(\sqrt{\alpha^2+1} - \alpha) - 1 + f_1(\alpha,\bar{\delta})} \qquad (A4.10)$$

where, $$f_1(\alpha,\bar{\delta}) = \frac{4\alpha^2}{\exp[(2\alpha+1)\bar{\delta}]}\left[\frac{\bar{\delta}}{(2\alpha+1)} + \frac{1}{(2\alpha+1)^2}\right] - \frac{(1+2\alpha\bar{\delta})}{\exp(2\alpha\bar{\delta})}$$

Equation A4.10 is the equation for the curve of neutral stability and is plotted in Figure A4-2. For a given $\bar{\delta}$, the critical (minimum) value of the Marangoni number occurs at $\alpha = 0$, and is given by

$$N_{Ma,cr} = \frac{2}{0.5(\bar{\delta}^2-0.5) + [\exp(-\bar{\delta})](\bar{\delta}+1)} \qquad (A4.11)$$

Using Equations A4.3 together with the expression for calculating the value of $\bar{\hat{c}}_i$ [D2], an estimate of the value of $\bar{\delta}$ for a given time of exposure, t, is given by (for $k_1 t > 3$)

$$e^{-\bar{\delta}} + \bar{\delta} \cong 2\sqrt{\frac{k_1 t}{\pi}} \qquad (A4.12)$$

It should be noted that the dimensional wavelength λ corresponding to a given value of α is given by

$$\lambda = \frac{2\pi}{\alpha}\sqrt{\frac{D_L}{k_1}} \qquad (A4.13)$$

For the sake of illustration consider a hypothetical system where:

$$\sigma = 10 \frac{\text{dyn cm}^2}{\text{gmole}} ;$$

$$\hat{a}_i = 3 \times 10^{-5} \frac{\text{gmole}}{\text{cm}^3} ;$$

$$\mu_L = 10^{-2} \text{ poise} ;$$

$$D_L = 10^{-5} \text{ cm}^2/\text{s} ;$$

and $$k_1 = 10^3 \text{ s}^{-1} .$$

In this case $N_{Ma} = 0.3$ and the value of $\bar{\delta}$ corresponding to a value of the

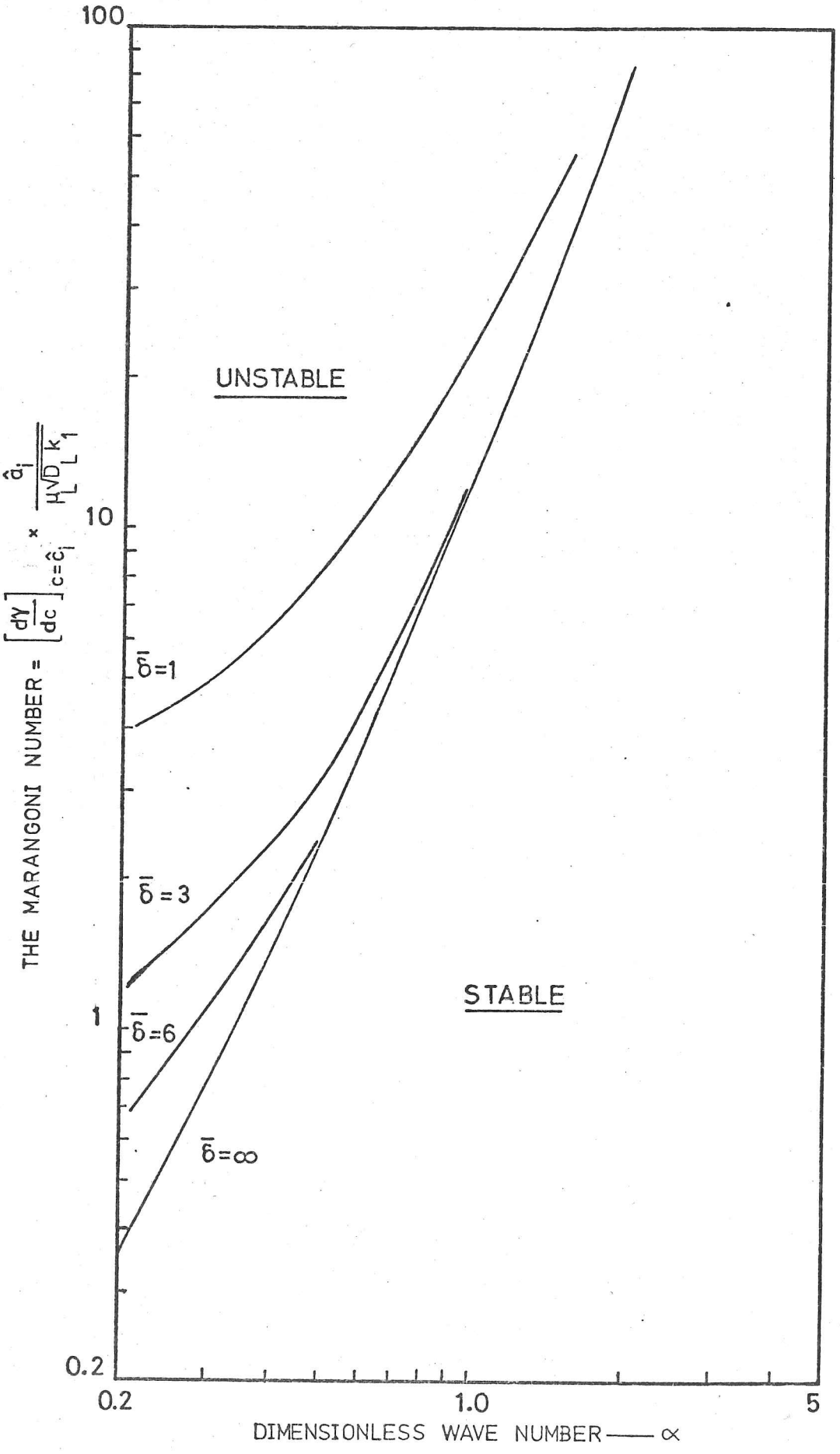

FIG. A4-2 THE CURVE OF NEUTRAL STABILITY—EQUATION A4.10

critical Marangoni number of 0.3 is equal to (Equation A4.11) 3.69. The system, according to the above analysis, will be unstable with respect to Marangoni instability after an exposure-time of roughly 10 milliseconds (for perturbations of infinitely large wavelength). It should be noted that for the systems encountered in practice, the wavelength of the largest possible disturbance is limited by the finite dimensions of the system.

NOMENCLATURE

N.B. : Symbols which make only a transitory appearance in the thesis have not been included in the following list since they are defined adequately in context.

$\underline{a}$	specific interfacial area, cm^2/cm^3
a, c, ... etc.	concentration of the species A, C, ... etc. in the liquid, $gmole/cm^3$
C	concentration of the solute in the liquid, $gmole/cm^3$
d	depth, or thickness, of the liquid layer, cm
D	solute diffusivity, cm^2/s
E_L	liquid-phase mass-transfer enhancement factor ($= k_L/k_L^*$), dimensionless
E_R	factor by which the rate of absorption is increased because of the reaction in the liquid phase
erf(z)	error function of z ($= \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2)du$)
exp(z)	exponential of z ($= e^z$)
G	gas flow rate, cm^3/s
H	Henry's-law constant, cm^3 atm/gmole
h	height of the exposed film, cm

k_1	first-order reaction rate-constant, s^{-1}
k_L	liquid-phase mass-transfer coefficient, cm/s
k_G	gas-phase mass-transfer coefficient, gmole/cm^2 s atm
K_G	overall gas-phase mass-transfer coefficient, gmole/cm^2 s atm
l	length of the laminar jet, cm
L	liquid flow rate, cm^3/s
N	stirrer speed, revolutions per minute (RPM)
N_{Ma}	Marangoni number, dimensionless
N_{Ad}	Adsorption number, dimensionless
N_{Sc}	Schmidt number, dimensionless
p	fluid pressure, dyn/cm^2 or dimensionless growth rate constant
R'	average rate of absorption, gmole/s
$\overline{R}$	average rate of absorption per unit interfacial area, gmole/cm^2 s
R_g	universal gas constant, cm^3 atm/gmole ^oK or erg/gmole ^oK
R_r	ratio of liquid phase resistance to the gas phase resistance in the absence of the Marangoni effect
s	fractional rate of surface renewal, $second^{-1}$
$\overline{s}$	average fractional rate of surface renewal, $second^{-1}$

t	exposure-time, s or defined by Equation 7.8
u, v, w	velocity components in the x, y, and z directions, respectively, cm/s
$\langle u_i \rangle$	defined by Equation 7.12
v	superficial velocity, cm/s or velocity, cm/s
V	packed volume, cm^3
wt. %	weight per cent
x_o	size of the cell, cm

Greek Letters

α	dimensionless wave number of the perturbations
γ	surface tension, dyn/cm
δ	defined by Equation A4.3
θ	exposure-time, s or time, s
λ	wavelength of the perturbations, cm
μ	viscosity, g/cm s
ν	kinematic viscosity, cm^2/s
ρ	density, g/cm^3
$\phi(t)$	surface age distribution function

Subscripts

b	in the bulk
i	interface
G	gas phase
L	liquid phase
s	at the surface

Superscripts

*	in the absence of the Marangoni effect
'	infinitesimal perturbations in the system variables (unless otherwise stated, e.g. R')
^	in the steady or pseudo-steady state
—	dimensionless variable (unless otherwise stated, e.g. $\overline{s}$, $\overline{R}$)

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